

Electrodeposition of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ Materials for Solar Cells

Final Report

24 April 1995—31 December 2001

Principal Investigator: R. Bhattacharya

CIS Team Members: A.M. Fernandez,
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and M. Contreras

*National Renewable Energy Laboratory
Golden, Colorado*



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TABLE OF CONTENTS

TABLE OF CONTENTS.....	i
EXECUTIVE SUMMARY	1
EXPERIMENTAL.....	4
1. Preparation of CIGS films using standard solutions.....	4
2. Preparation of CIGS Films Using Buffer Solutions	5
RESULTS AND DISCUSSION.....	7
CONCLUSIONS.....	14
REFERENCES	15
ATTACHMENTS.....	17

EXECUTIVE SUMMARY

This report will present and discuss the research performed during a 6-year period (4/24/95 to 12/31/01) under support of Contract FIA-95-1326 between NREL and Davis, Joseph & Negley. The total budget amount during this 6-year period was \$737,942. The contract, “Electrodeposition of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ Materials for Solar Cells,” was integrally linked with a much larger effort in CIGS at NREL supported by the DOE to develop the scientific understanding of this materials system, solar cells, and processes that can address the goals of the National Photovoltaics Program [1]. Through DOE support, the investigators developed much of the technology and device fabrication infrastructure applied to electrodeposited (ED) materials.

The electrodeposition process is simple and fast, and can synthesize multinary precursors for subsequent processing into $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) thin-film absorbers for solar cells. The device fabricated using electrodeposited CIGS precursor layers resulted in total-area conversion efficiencies up to 15.4% [2]. As-deposited precursors are Cu-rich CIGS. Additional In, Ga, and Se (up to 50%) are added to the precursor films by physical vapor deposition (PVD) to adjust the final semiconductor film composition to about $\text{Cu}_{0.95}\text{In}_{0.75}\text{Ga}_{0.25}\text{Se}_2$. The electrodeposited device parameters are compared with those of an 18.8% PVD device [3]. The tools used for comparison are current-voltage, capacitance-voltage, and spectral response characteristics. The individual parameters of the device prepared from electrodeposited precursor films showed no significant deterioration from those of the PVD CIGS cells.

We also developed a buffer-based electrodeposition bath under this subcontract. Using buffer solution enhances the stability of the electrodeposition process, and no metal oxides or hydroxides precipitate out of the solution. The buffer-based bath also deposits more gallium in the precursor films. As-deposited precursors are stoichiometric or slightly Cu-rich CIGS. Only a minimal amount (5%-10% of total materials) of indium was added to the electrodeposited precursor films by physical vapor deposition to obtain a 9.4%-efficient device.

In general, the films and devices have been characterized by inductively-coupled plasma spectrometry, Auger electron spectroscopy, X-ray diffraction, electron-probe microanalysis, current-voltage, capacitance-voltage, and spectral response.

During the period of this research, the preferred communication has been extensive publications and presentations in journals and technical conferences, as shown in the bibliography. This report will not reproduce the details already published. It comprises a brief guide through existing publications and references, adding only limited detail as needed to bridge gaps in prior work. Selected copies of the work published under the contract are attached for convenience.

INTRODUCTION

Photovoltaic solar cells are a very attractive source of clean energy. At present, the photovoltaic industry primarily uses wafers of single-crystal and polycrystalline silicon, which generally have a wafer thickness in the range of 100–300 μm . The wafers must go through several processing steps and then be integrated into a module. The high material and processing costs make these modules relatively expensive. Thin-film solar cell technology is a promising alternative to silicon solar cell technology. $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) has become one of the leaders in this field. Its large optical absorption coefficient, due to a direct energy gap, permits the use of thin layers (1–2 μm) of active material. CIGS solar cells are also known for their long-term stability [4]. All these qualities have brought CIGS-based devices to the forefront in solar cell applications.

The recent record-breaking 18.8%-efficient [3] CIGS-based device fabricated in our research laboratory is based on a multistep process using physical vapor deposition (PVD). The PVD method is an excellent tool for understanding film growth and for developing models, but challenging to scale up. Sputtering techniques are suitable for large-area deposition; however, they require expensive vacuum equipment and sputtering targets. Electrodeposition (ED) is a highly suitable preparation method to obtain low-cost precursor films. In 1983, we demonstrated for the first time that CIS could be prepared by the electrodeposition process [5]. Since then, several groups including us have investigated the electrodeposition of CIGS materials [6-10]. The ED process could provide: (a) very good-quality film with very low capital investment; (b) a low-cost, high-rate process; (c) use of very low-cost (e.g., low-purity salts, solvents) starting materials because of automatic purification of the deposited materials during plating; (d) a large-area, continuous, multicomponent, low-temperature deposition method; (e) deposition of films on a variety of shapes and forms (wires, tapes, coils, and cylinders); (f) controlled deposition rates and effective material use (up to 95%); and (g) minimum waste generation (solution can be recycled).

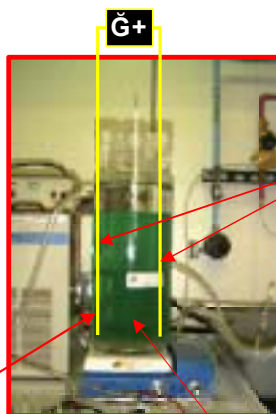
EXPERIMENTAL

1. Preparation of CIGS films using standard solutions

ED precursor films are deposited from an acidic bath (pH~2) containing 0.02-0.05M CuCl_2 , 0.04-0.06M InCl_3 , 0.01-0.03M H_2SeO_3 , 0.08-0.1M GaCl_3 , and 0.7-1M LiCl dissolved in deionized water. The range of bath compositions and process conditions is presented in detail in U.S. patents 5,871,630, 5,730,852, and 5,804,054 [11-13]. Cu, In, Ga, and Se are co-deposited from the solution at room temperature onto the substrate in a vertical cell, as shown in Figure 1, in which the electrodes are suspended from the top of the cell. The ED precursors are prepared in a three-electrode cell in which the reference is a platinum pseudo-reference, the counter is platinum gauze, and the working electrode is the substrate. The depositions are performed by a non-stirring diffusion process (movement of a species under the influence of a gradient of chemical potential, i.e., a concentration gradient).

Electrodeposition Process

Electrical variables: ¥ Potentials (V) (half-cell potential, overpotential, E)
¥ Current (I)
¥ Coulombs (Q)



Electrode variables:
¥ Material
¥ Surface area
¥ Geometry
¥ Surface condition

Electrical variables:
¥ Mode (diffusion, convection)
¥ Surface concentration
¥ Adsorption

Solution variables:
¥ Bulk concentration of electroactive (C_O , C_R)
¥ Concentrations of other species (electrolyte, pH, E)
¥ Solvent

Figure 1. The electrodeposition set-up.

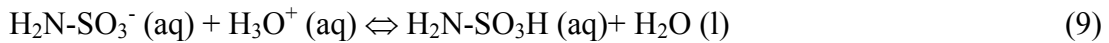
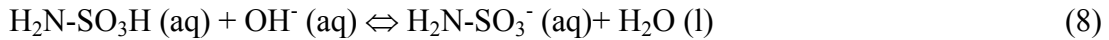
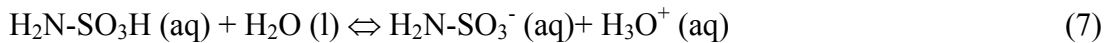
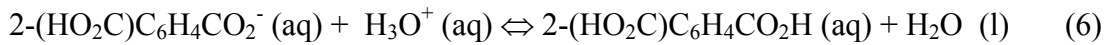
Compositions of the as-deposited precursors are determined by inductively coupled plasma (ICP) analysis. The as-deposited precursors are Cu-rich, and additional In, Ga, and Se are added by PVD to adjust their final composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$. During this step, the substrate temperature is maintained at $560^\circ\pm 10^\circ\text{C}$. These target compositions are Cu poor, as determined and optimized under the DOE-supported program [3, 14]. The photovoltaic devices are then completed with a 50-nm layer of chemically deposited CdS, 50 nm of RF-sputtered intrinsic ZnO, 350 nm of Al-doped ZnO, and bilayer Ni/Al top contacts deposited by e-beam using the process optimized for PVD devices made in our laboratories that have demonstrated efficiencies up to 18.8% [3]. Finally, a 100-nm layer of MgF_2 is deposited to minimize reflection. The final configuration for all devices reported in this paper is $\text{MgF}_2/\text{ZnO}/\text{CdS}/\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2/\text{Mo}/\text{glass}$.

2. Preparation of CIGS Films Using Buffer Solutions

The electrodeposition of CIGS films (pH ~ 2) on cathodes is most likely caused by the combination of electrochemical and chemical reactions as follows:

	E^0 vs. SHE	
$\text{Cu (II)} + 2e \rightarrow \text{Cu}$	0.342 V	(1)
$\text{In (III)} + 3e \rightarrow \text{In}$	-0.338 V	(2)
$\text{Ga (III)} + 3e \rightarrow \text{Ga}$	-0.549 V	(3)
$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4e \rightarrow \text{Se} + 3\text{H}_2\text{O}$	0.74 V	(4)
$\text{Cu, In, Ga, Se} \rightarrow \text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$	Chemical reaction	(5)

The electrodeposition is carried out in pH buffer “hydrion” (pH 3) that is a mixture of sulfamic acid and potassium biphthalate [15]. The role of the buffer solution could be understood by the following reactions:



The composition of the as-deposited electrodeposited precursors as analyzed by ICP analysis was between $\text{CuIn}_{0.68}\text{Ga}_{0.19}\text{Se}_{1.94}$ and $\text{CuIn}_{0.51}\text{Ga}_{0.35}\text{Se}_{1.94}$. Previously, the precursor compositions prepared in the absence of buffer solution (which resulted in a 15.4%-efficient device) was between $\text{CuIn}_{0.32}\text{Ga}_{0.01}\text{Se}_{0.93}$ and $\text{CuIn}_{0.35}\text{Ga}_{0.01}\text{Se}_{0.99}$. The new electrodeposition bath that includes a buffer solution was stable for several weeks, and no metal oxides or hydroxides precipitated out of solution. The present deposition bath also allows electrodepositing more gallium in the precursor films. This buffer-based electrodeposition bath provides an improved deposition process for producing stoichiometric CIGS precursor thin films with enough concentration of each element that minimal, if any, additional vapor deposition processing is required. The CIGS absorber layers are prepared from the present precursor films by adding only about 2000 Å of indium and selenium by the PVD step. The best devices prepared from these precursor films were about 9.4% efficient (Figure 2). Current-voltage (I-V) characterization is carried out at AM1.5 illumination (1000 W/m^2 , 25°C). The fill factor and open-circuit voltage for these devices were only about 64% and 0.413 V, respectively.

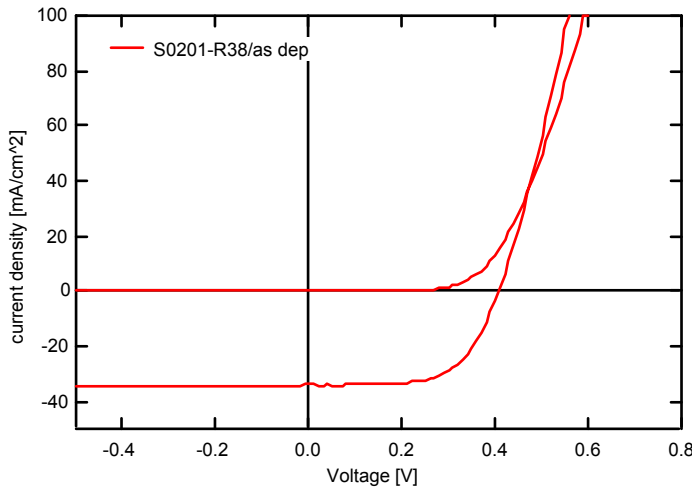


Figure 2. Current-voltage characteristic of a device prepared from electrodeposited precursor film. (Area = 0.43 cm^2 ; $V_{oc} = 0.413 \text{ V}$; $J_{sc} = 35.41 \text{ mA/cm}^2$; FF = 64%; Efficiency = 9.4%).

RESULTS AND DISCUSSION

The morphology of the precursor films and devices were investigated by scanning electron microscopy (SEM). Figure 3 show the SEM image of the representative ED precursor films. As the micrograph shows, the as-deposited precursor films are densely packed and have very small particle size. Figures 4 and 5 are SEM micrographs of the representative PVD device and ED device, respectively. The morphology of the ED device differs significantly from the PVD device. The PVD device has larger grain-size compared with the ED device. In some instances, we also noticed some significant lift-off at the Mo/CIGS interface for ED devices prepared from Cu-rich precursor films, as shown in Fig. 5. The precursor deposition conditions and morphology are described in our earlier papers [6,16].

The device prepared from ED precursor film was examined by Auger analysis. The PVD addition of the In, Ga, and Se is observed to produce a nonuniform Ga/(In+Ga) distribution. An Auger analysis of the cell is presented in Fig. 6. The Auger analysis shows nonuniform distribution of Ga in the absorber. The Ga hump is not helpful for hole collection. We expected to improve the device efficiencies by optimizing the Ga distribution in the absorber layers. The optimized layers should have less Ga in the front and more Ga on the back, which facilitates hole collection. We were not able to obtain such an optimized device.

Figure 7 shows the current density vs. voltage (J-V) curves of the best devices prepared from ED film completed with a 50% PVD step. The I-V characterization was carried out at AM1.5 spectrum (ASTM E 892-87 Global), in which the intensity of illumination was 1000 W/m^2 . The solar cell made from the ED precursor material has device efficiencies of 15.4%. The quantum efficiencies (QE) of the cells under illumination (1000 W/m^2) are shown in Fig. 8. This figure indicates that the bandgap, E_g , of the ED cell is 1.20 eV [$\text{Ga}/(\text{In}+\text{Ga}) = 0.39$].

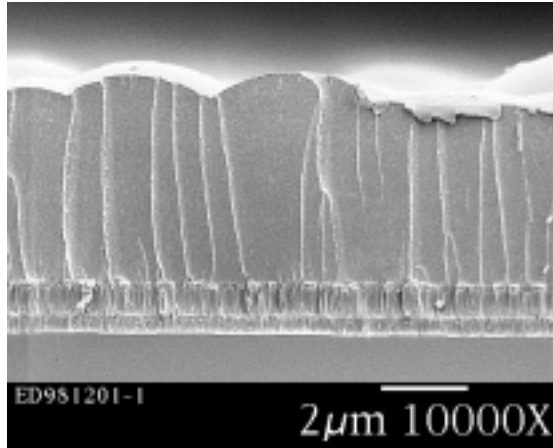


Figure 3. SEM image of an electroplated CIGS precursor film.

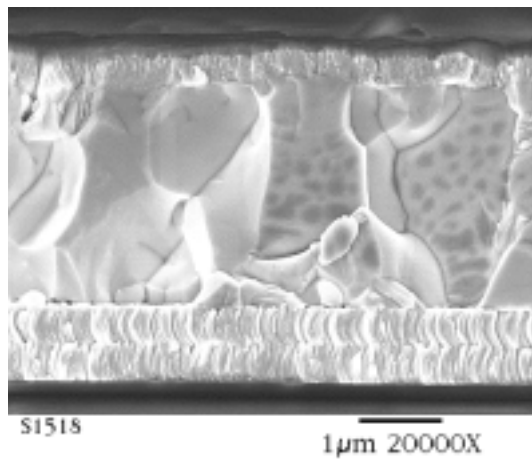


Figure 4. SEM image of a PVD device.

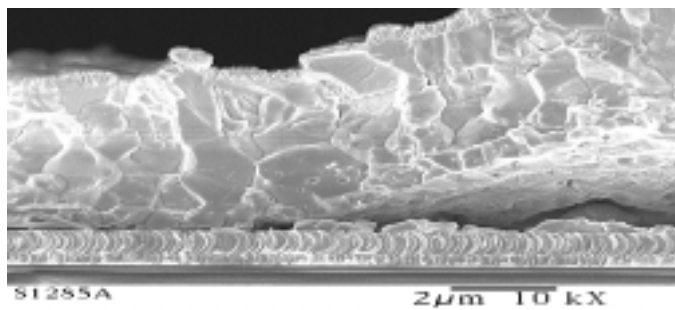


Figure 5. SEM image of a representative ED device.

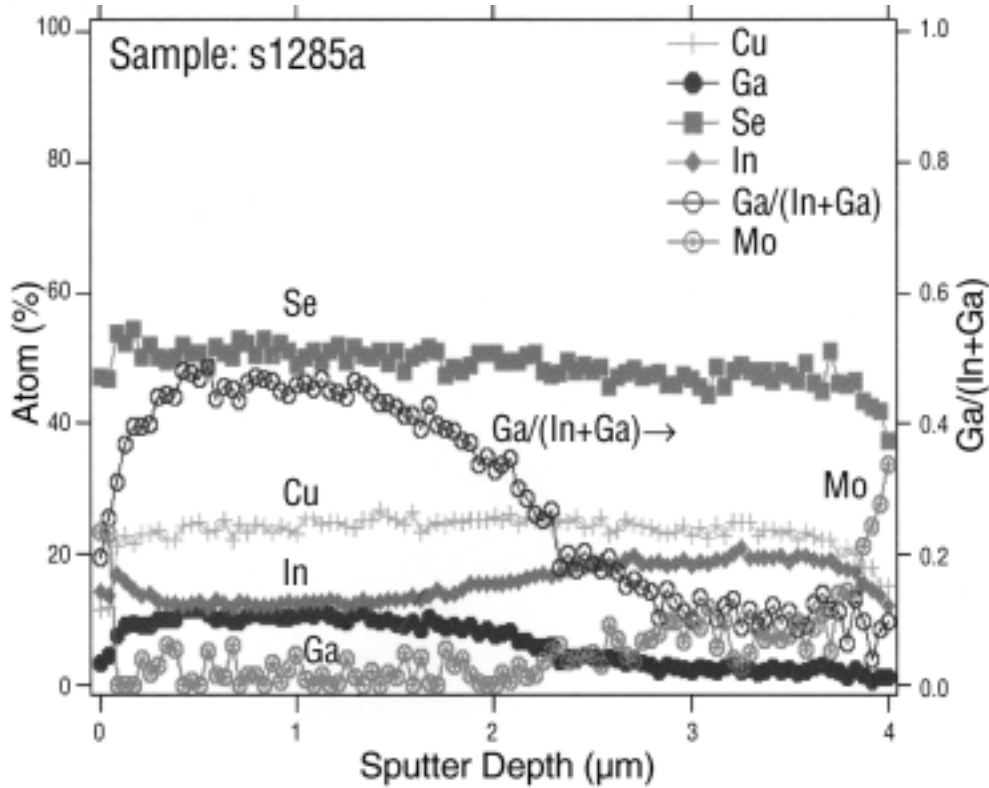


Figure 6. Auger analysis of ED device (15.4%).

We compared the 15.4%-efficient ED cell with the 18.8%-efficient PVD cell [17]. The device prepared from ED precursor film seems to compare well with the 18.8%-efficient PVD device in open-circuit voltage (V_{oc}), and less well in short-circuit current (J_{sc}); however, because of the bandgap difference of 80 mV, one would expect a higher voltage in the ED device if all other qualities of the junction were equal. The capacitance-voltage (C-V) results show fairly uniform dopant density of 10^{16} cm^{-3} for the ED cell. These are both within the typical range for high-quality CIGS cells.

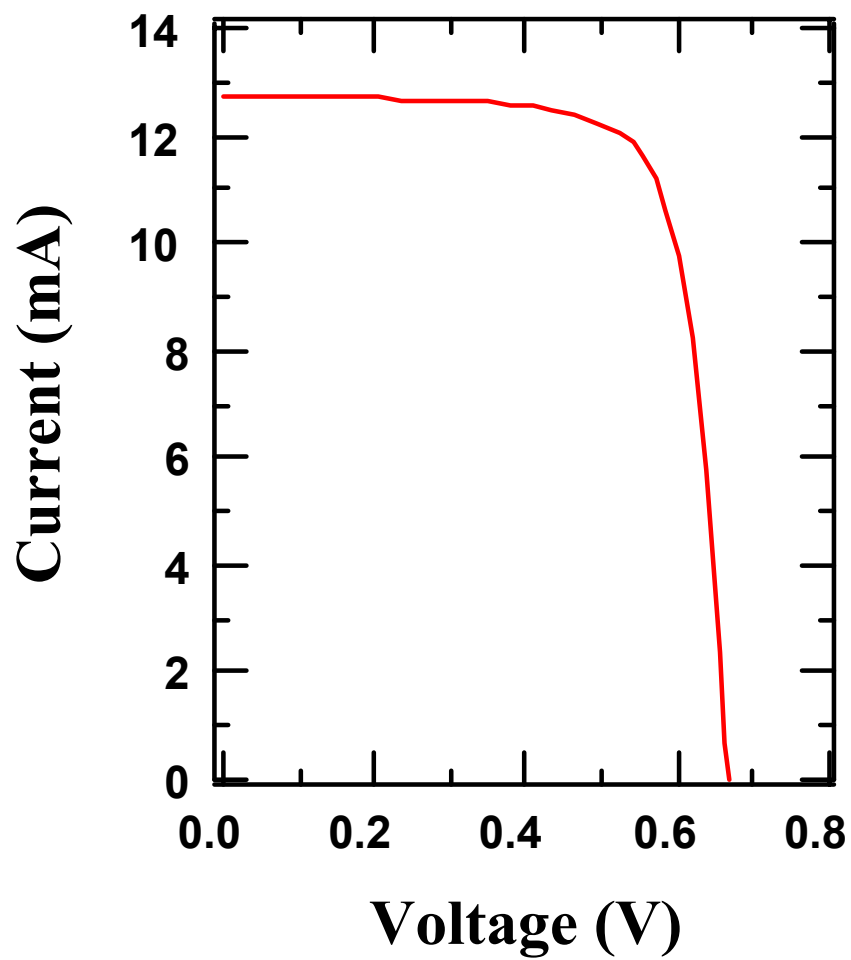


Figure 7. I-V characteristics of an ED device ($V_{oc} = 0.666$ V, $I_{sc} = 12.76$ mA, $J_{sc} = 30.51$ mA/cm², Fill Factor = 75.56%, Efficiency = 15.4%).

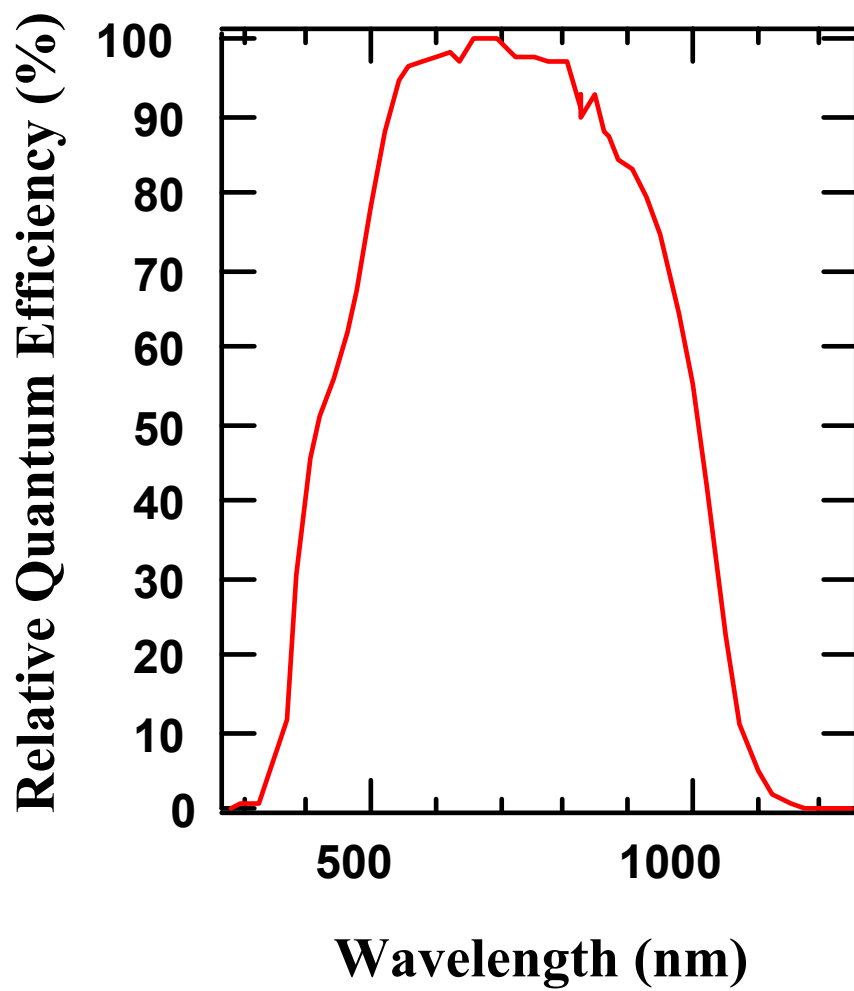


Figure 8. Quantum-efficiency data for the 15.4%-efficient ED device.

Table 1. Parameters of the Devices Prepared from Electrodeposition Precursor (ED Device) and also from Physical Vapor Deposition (PVD Device)

Cell	ED device	PVD device
Ga/(In+Ga)	0.4	0.28
Area [cm ²]	0.418	0.432
V _{oc} [V]	0.666	0.678
J _{sc} [mA/cm ²]	30.51	35.2
V _{max} [V]	0.554	0.567
J _{max} [mA/cm ²]	27.8	34.5
FF [%]	75.6	78.6
r _{shunt} [Ω -cm ²]	2000	10000
R _{series} [Ω -cm ²]	0.3	0.2
Ideality Factor [A]	1.8	1.5
Depletion Width [μ m]	0.2	0.5
Hole Density [cm ⁻³]	1x10 ¹⁶	1x10 ¹⁶
Bandgap [eV]	1.20	1.12
Efficiency [%]	15.4	18.8

Electrical characterization data of the devices prepared from ED precursors are listed in Table 1. Electrical characterization of the devices included I-V in the dark and under AM 1.5, 100-mW/cm² illuminated conditions, QE, and C-V measurements. Resistance and diode-quality parameters were extracted from the J-V data. The shunt resistance (r_{shunt}) is a measure of leakage and is indicated by the slope of the J-V curve in reverse bias. The device prepared from ED precursor demonstrates slight leakage in the light, with shunt resistances of 1000–2000 ohm-cm², as compared to the PVD device, with a higher value of 10,000 ohm-cm². Series resistance (R_{series}) is indicative of the quality of the bulk material, whereas the diode-quality factor (A) indicates whether there is significant excess forward current through recombination states and hopping paths. Both of these quantities are extracted from the region of the curve between the maximum power point and open-circuit voltage. As with shunting, the series resistance is not a significant factor for any of the cells.

Table 2. Comparison of Primary ED Parameters with the Record 18.8%-Efficient PVD Cell

	ED vs. PVD (adjusted for E_g)
Efficiency Difference [%]	3.4 (3.4)
Difference from V_{oc} [%]	0.3 (1.4)
Difference from J_{sc} [%]	2.3 (1.2)
Difference from FF [%]	0.8 (0.8)

Table 2 shows the relative contributions of the primary solar-cell parameters to the lower performance seen in the ED cell. The differences in voltage and current can be misleading if cells of different bandgap are compared; hence note the second values in parenthesis, which are the performance differences for a common bandgap. The second values in comparison with the PVD device show, (a) somewhat smaller voltages attributed to the excess forward current, (b) somewhat smaller currents primarily due to lower collection of carriers created by the more penetrating infrared photons, and (c) a small fill-factor difference for the ED cell. In summary, the individual parameters of the device prepared from electrodeposited precursor films showed no significant deterioration from those of the PVD CIGS cells.

CONCLUSIONS

Devices fabricated using ED CIGS precursors resulted in efficiencies of 15.4% [2]. The quality of CIGS-based films and devices prepared from the solution-based ED precursor film is very promising. The device-quality ED precursor films are Cu-rich CIGS films. Additional In and/or Ga, and Se are added to the precursor films by PVD to adjust the final composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$. The solution-based precursor process will be more attractive for CIGS solar cell fabrication if we can eliminate the PVD step. We worked toward this goal. Our near-term goal was to minimize the PVD step to only a few nanometer depositions while maintaining the high efficiency (>14% efficiency). We added up to 50% material by PVD to obtain 15.4%-efficient devices. The optimization of the deposition condition using buffer solution helped to increase the In and Ga concentration in the precursor films, which cut down the PVD step to only 10%–20% of total materials, but maximum efficiency obtained for such devices was 9.4% [15]. The electrodeposition processing will be attractive if the following tasks are accomplished: (1) The development of a processing condition that will lead to uniform gallium distribution, thus improving the device efficiency; (2) Demonstration of >14% device efficiency on large-area substrates (minimum recommended area = 8 in. x 8 in.); and (3) Elimination of the PVD step while maintaining the device efficiency >14%.

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3. R. N. Bhattacharya, F. Hasoon, H. Wiesner, J. Keane, K. Ramanathan, and R. Noufi, "Preparation of Copper-Indium-Gallium-Diselenide Films for Solar Cells," Patent Number: 5,804,054, September 8, 1998.

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United States Patent [19]

Bhattacharya et al.

[11] Patent Number: 5,730,852

[45] Date of Patent: Mar. 24, 1998

[54] PREPARATION OF CUXINYGAZSEN (X=0-2, Y=0-2, Z=0-2, N=0-3) PRECURSOR FILMS BY ELECTRODEPOSITION FOR FABRICATING HIGH EFFICIENCY SOLAR CELLS

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[58] Field of Search 205/103-104, 205/192, 915, 239; 437/5, 108, 111; 427/76; 136/260, 264, 265; 257/184; 204/DIG. 8

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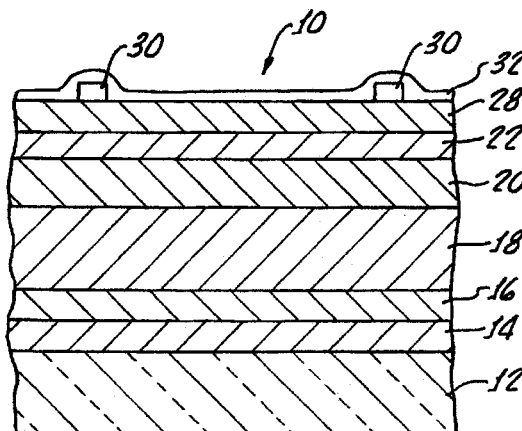
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[57] ABSTRACT

High quality thin films of copper-indium-gallium-diselenide useful in the production of solar cells are prepared by electrodepositing at least one of the constituent metals onto a glass/Mo substrate, followed by physical vapor deposition of copper and selenium or indium and selenium to adjust the final stoichiometry of the thin film to approximately Cu(In, Ga)Se₂. Using an AC voltage of 1-100 KHz in combination with a DC voltage for electrodeposition improves the morphology and growth rate of the deposited thin film. An electrodeposition solution comprising at least in part an organic solvent may be used in conjunction with an increased cathodic potential to increase the gallium content of the electrodeposited thin film.

20 Claims, 2 Drawing Sheets



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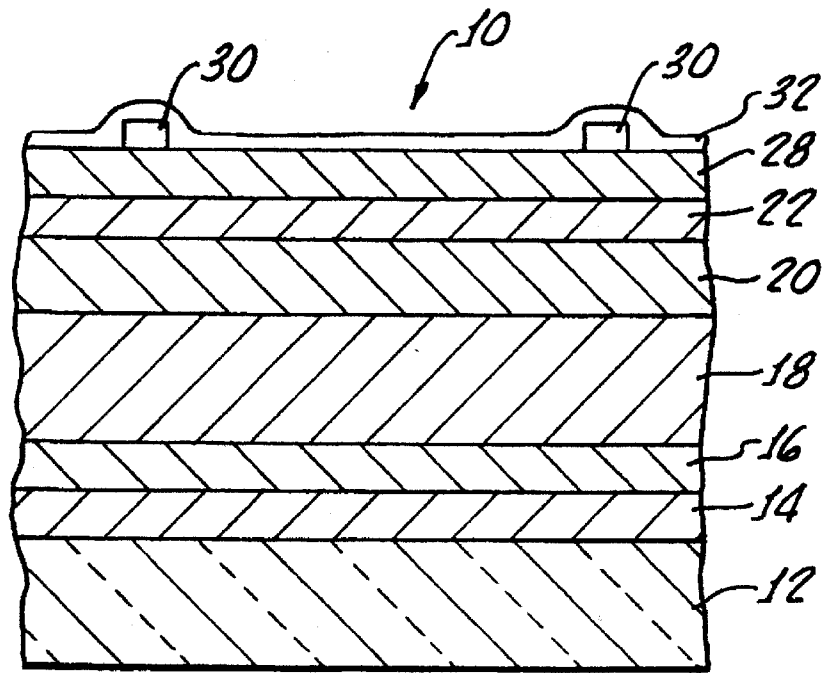


FIG. 1.

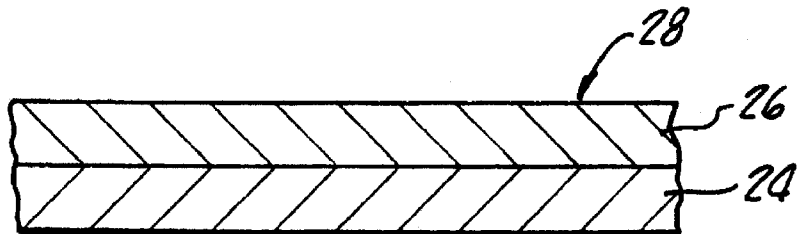
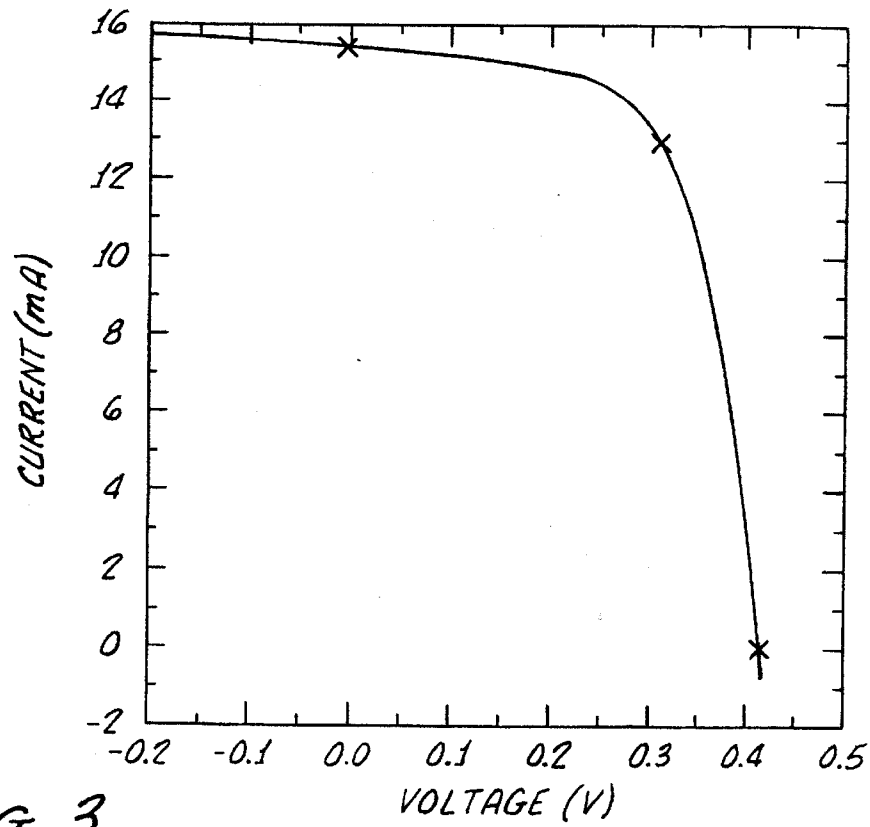
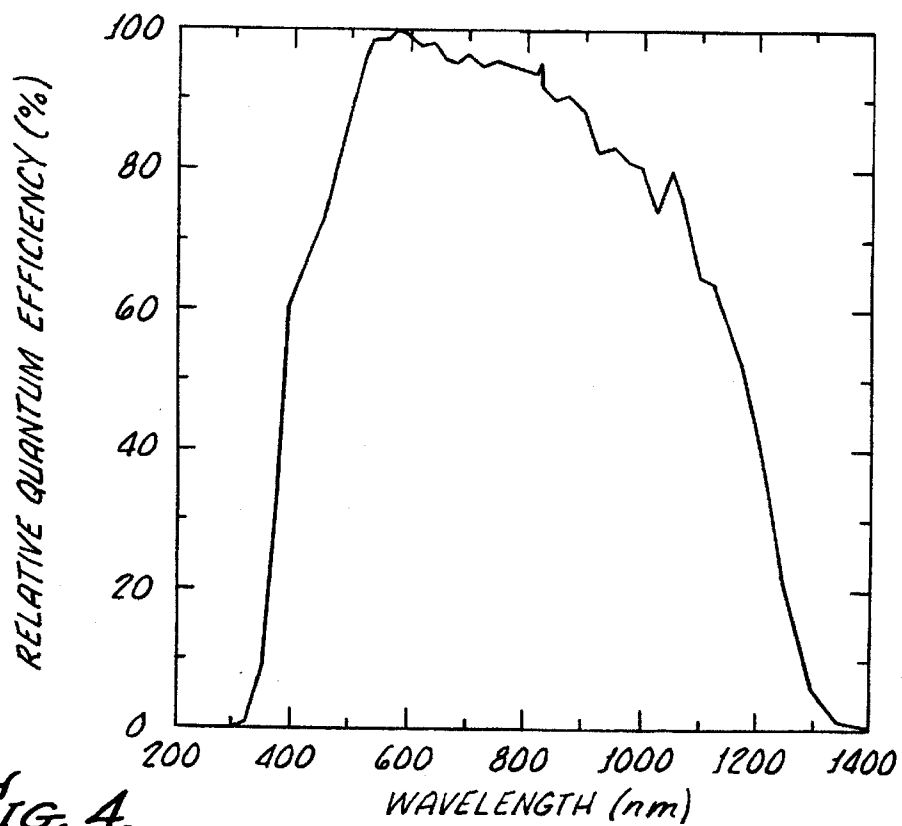


FIG. 2.

FIG. 3.FIG. 4.

PREPARATION OF CUXINYGAZSEN (X=0-2, Y=0-2, Z=0-2, N=0-3) PRECURSOR FILMS BY ELECTRODEPOSITION FOR FABRICATING HIGH EFFICIENCY SOLAR CELLS

The government has rights in this invention pursuant to National Renewable Energy Laboratory (NREL) contract No. 1326.

RELATED APPLICATIONS

This application is a continuation-in-part of provisional application Ser. No. 60/004269, filed Sep. 25, 1995.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of the present invention relates to the preparation of thin film semiconductor devices. More particularly, the present invention relates to electrodeposition of copper-indium- gallium-selenide films for solar cells.

2. Description of the Related Art

Chalcopyrite ternary thin films of copper-indium-diselenide (CuInSe_2) and copper-indium- gallium-diselenide ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$), both of which are generically referred to as Cu(In,Ga)Se_2 , CIGS, or simply CIS, have become the subject of considerable interest and study for semiconductor devices in recent years. Sulphur can also be, and sometimes is, substituted for selenium, so the compound is sometimes also referred to even more generically as Cu(In,Ga)(Se,S)_2 so as to encompass all of these possible combinations. These devices are also referred to as I-III-VI₂ devices according to their constituent elemental groups.

These devices are of particular interest for photovoltaic device or solar cell absorber applications. For photovoltaic applications, the p-type CIGS layer is combined with an n-type CdS layer to form a p-n heterojunction CdS/CIGS device. The direct energy gap of CIGS results in a large optical absorption coefficient, which in turn permits the use of thin layers on the order of 1-2 μm . An additional advantage of CIGS devices is their long-term stability.

Various methods have been reported for fabricating CIGS thin films. Some of the earliest techniques involved heating copper and indium on a substrate in the presence of a selenium-containing gas, including H_2Se . The heating of copper and indium films in the presence of a selenium-containing gas is known as selenization. One drawback to selenizing with H_2Se is that H_2Se gas is highly toxic, thus presenting serious hazards to humans in large scale production environments.

In U.S. Pat. No. 5,045,409, Eberspacher et al. disclose depositing copper and indium films by magnetron sputtering, and depositing a selenium film by thermal evaporation, followed by heating in the presence of various gases. Other methods for producing CIS films have included Molecular Beam Epitaxy, electrodeposition either in single or multiple steps, and vapor deposition of single crystal and polycrystalline films.

Although vapor deposition techniques have been used to yield solar cells with efficiencies as high as seventeen percent (17%), vapor deposition is costly. Accordingly, solar cells made by vapor deposition have generally been limited to devices for laboratory experimentation, and are not suitable for large scale production. On the other hand, thin film solar cells made by electrodeposition techniques are generally much less expensive. However, solar cells produced by electrodeposition generally suffer from low efficiencies. For

example, in *Solar Cells with Improved Efficiency Based on Electrodeposited Copper Indium Diselenide Thin Films*, ADVANCED MATERIALS, Vol. 6 No. 5 pp 379-381 (1994), Guillemoles et al. report solar cells prepared by electrodeposition with efficiencies on the order of 5.6%.

SUMMARY OF THE INVENTION

Accordingly, it is a general object of this invention to provide an improved process for fabricating high quality thin film Cu(In,Ga)Se_2 solar cells.

It is also an object of this invention to provide low cost, high quality thin film solar cells having high conversion efficiencies.

It is a further object of this invention to provide a process for producing Cu-In, Cu-Se, Cu-In-Se, and Cu-In-Ga-Se thin films that have applications in solar and non-solar cells.

It is a still further object of this invention to provide a process for electrodepositing a gallium-containing thin-film solar cell precursor.

To achieve the foregoing and other objects and advantages in accordance with the purpose of the present invention, as embodied and broadly described herein, the process of this invention includes electrodepositing a layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$), preferably using direct current in combination with alternating current, followed by vapor depositing additional copper and selenium or indium and selenium to adjust the final composition very close to stoichiometric Cu(In,Ga)Se_2 . This unique two-step film deposition process allows photovoltaic precursor films to be deposited by inexpensive electrodeposition, and then adjusted using the more expensive but more precise technique of physical vapor deposition to bring the final film into the desired stoichiometric range. Solar cells may then be completed as for example by chemical bath deposition (CBD) of CdS followed by sputtering of ZnO, and addition of bi-layer metal contacts as well as optional anti-reflective coating. A solar cell made according to the present process has exhibited a device efficiency of 9.44%.

Additional objects, advantages, and novel features of the present invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a CIGS photovoltaic device prepared according to the present invention.

FIG. 2 is a cross sectional view of the conducting zinc oxide layer 28 shown in FIG. 1.

FIG. 3 is the current vs. voltage performance plot of a CdS/ CuInSe_2 solar cell prepared according to Example 3 of the present invention.

FIG. 4 is a plot of relative quantum efficiency versus wavelength for the CdS/ CuInSe_2 solar cell of Example 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention includes an essentially two-step process for fabricating high quality, low cost thin film CIGS semiconductor devices that exhibit photovoltaic characteristics and are especially adaptable for solar cell applications. In the first step, a photovoltaic precursor film of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) is electrodeposited on a substrate such as glass coated with molybdenum. This first step may include a unique process and

electrodeposition bath for electrodepositing gallium concurrently with other elements, as well as the unique use of an alternating current in conjunction with a direct current.

The second step is physical vapor deposition of either Cu+Se or In+Se, either alone or in combination with Ga. In this second step the composition of the overall film is carefully controlled so that the resulting thin film is very close to stoichiometric Cu(In,Ga)Se₂. Both of these steps may be performed on substrates having large surface areas. Accordingly, the process of the present invention allows large area, high efficiency solar cells to be economically produced.

Referring now to FIG. 1, CdS/CIGS photovoltaic device 10 includes a substrate 12 which may be, for example, soda-lime silica glass or amorphous 7059 glass. Substrate 12 further includes a back contact layer 14 of molybdenum, about 1-2 μ m thick. The molybdenum may be deposited using DC sputtering from a rotating cylindrical magnetron target (CMAG). To improve adhesion between the Mo layer 14 and the precursor film to be deposited, an additional adhesion layer 16 of copper may also be deposited as by electrodeposition. After Mo layer 14 and optional copper adhesion layer 16 have been deposited, the substrate should be degreased as for example with propanol and dried in flowing nitrogen gas.

A photovoltaic precursor film 18 is then deposited by electrodeposition. The precursor film contains one or more of the elements copper, indium, gallium, and selenium. Electrodeposition is generally a less expensive method of depositing these metals than vapor deposition. However, it is not possible to control the ratios of metals deposited during electrodeposition as precisely as desired. Consequently, prior CIGS layers deposited entirely by electrodeposition produced low conversion efficiencies. In the present invention, the electrodeposition step is integrated with the vapor deposition step that follows. This allows precursor films to be deposited in bulk using an economical electrodeposition step, followed by a vapor deposition step to carefully control the final ratios. This results in economical production yet high efficiencies of the resulting cell. The composition of precursor film 18 is generally denoted as Cu_xIn_yGa_zSe_n (x=0-2, y=0-2, z=0-2, n=0-3). The metal precursor film 18 should be deposited to about 1-3 μ m thick, with thickness being controlled by coulometric measurements.

It has been found that electrodepositing the films using an AC voltage in addition to a DC voltage produces improved results. An AC voltage improves the morphology of the film. It is also believed that the AC voltage improves nucleation (growth) of the thin film by allowing additional nucleation centers to be created. For an entirely aqueous plating solution, the applicable DC voltage range is approximately 1-5 VDC, with a preferred voltage of approximately 2 VDC. Improved results may be obtained by superimposing an AC voltage of 0.2-5.0 VAC at 1-100 KHz, with preferred values of approximately 0.3-1.0 VAC at 10-30 KHz. A value of approximately 0.45 VAC at approximately 18.1 KHz was found to yield good results. The plating solution is adjusted to have a pH of approximately 1.0 to 4.0, and more preferably to about 1.4 to 2.4. The plating solution should preferably be at about 10° C. to 80° C., and more preferably at about 24° C. Adding a supporting electrolyte to the plating bath can additionally increase the conductivity of the plating solution, allowing for a further increase in the electrodeposition rate. Salts such as NaCl, LiCl, or Na₂SO₄ have been found to be suitable supporting electrolytes for use with certain embodiments of the present invention.

In completely aqueous solutions, electrolysis of water molecules begins to occur to an undesirable extent at approximately 2-3 volts. The resulting O²⁻ and OH⁻ ions combine with deposition metal ions or deposited metal to form unwanted metal oxides and hydroxides on the precursor film 18. To overcome this disadvantage, the water in the plating solution may be either partially or completely replaced by one or more organic solvents such as dimethyl sulfoxide (DMSO). Increasing the organic solvent content of the electrodeposition solution allows the cathodic potential to be increased without unacceptable increases in metal oxide and hydroxide formation rates. The increased cathodic potential increases the deposition rate of the precursor films. An additional advantage is that increasing the cathodic potential increases the deposition rate of gallium relative to the deposition rates of other deposited metals. Therefore, using a solution containing one or more organic solvents allows the cathodic potential to be selected from a wider range so as to achieve a more desired stoichiometry of the as-deposited precursor film 18. When an organic solvent is used, the preferred cathodic potential is approximately 3-10 VDC and 0.2-5.0 VAC at approximately 1-100 KHz. Values of approximately 5 VDC and 0.45 VAC at approximately 18.1 KHz were found to yield good results.

If desired, a second electroplating solution may be employed to adjust the stoichiometry of the electrodeposited film prior to the vapor deposition phase. For example, a first electrodeposition step may produce a CIGS precursor film with less gallium than optimally desired. Although the gallium content can be increased during the vapor deposition phase, it may be less expensive to deposit a certain amount of gallium using a second electrodeposition solution to make a coarse stoichiometric adjustment prior to proceeding to fine stoichiometric adjustment at the vapor deposition step. Another potential motivation for using a second electrodeposition solution is to achieve a composition gradient in the deposited film, as suggested by U.S. Pat. No. 4,335, 266 issued to Mickelsen et al. which is hereby incorporated by reference for its teachings of composition-graded CIGS thin films for solar cell and other applications. Yet another way of achieving composition grading during electrodeposition is to vary process parameters such as cathodic potential, ionic concentrations, pH, or temperature, as electrodeposition proceeds.

Several examples of electrodeposited photovoltaic precursor films fabricated according to the present invention are given. These examples include In-Se, Cu-Se, and Cu-In-Se precursor films. For these precursor films, Ga should be added to raise the energy gap. The Ga may be added by a separate electrodeposition step, though is preferably added at the vapor deposition step by vaporizing elemental gallium. An example is also given of a novel solution and process that allows Ga to be electrodeposited along with other precursor constituents, to produce a Cu-In-Ga-Se precursor film electrodeposited in a single step. The solution includes ions of each of the elements of copper, indium, gallium, and selenium. These ions may be supplied in the form of dissolved metal salts.

After the precursor film 18 has been electrodeposited it should be cleaned. A suitable method is to rinse precursor film 18 with deionized water and dry it in flowing nitrogen gas. After precursor film 18 has been cleaned, an additional layer 20 of In+Se or Cu+Se, either alone or in combination with gallium, is deposited by physical vapor deposition to adjust the final film composition to the ratios of approximately Cu=1-1.2:(In,Ca)=1-1.2:Se=2-2.5, and most preferably to approximately 1:1:2. By controlling the ratio of

In/Ga the energy gap between the CdS and the CIGS layers can be adjusted to the optimal or nearly optimal value. An energy gap of approximately 1.45 eV is considered optimal for terrestrial solar energy conversion, and is achieved by an In/Ga ratio of approximately 3:1. The substrate (precursor film) temperature should be 300° C. to 600° C. during PVD, and preferably about 550° C.

After PVD, the films should then be annealed. Annealing improves the homogeneity and quality of the films. A high quality CIGS film is one that does not exhibit an excessive amount of copper nodules, voids, or vacancies in the film which would reduce conversion efficiencies. Annealing the films at 250° C. to 500° C. in a vacuum, followed by slow cooling at a rate of approximately 3° C./min to avoid thermal shock was found to yield good results. Because selenium has a much higher vapor pressure than either copper, indium, or gallium, selenium may be lost from the film during the high temperature steps of vapor deposition and annealing. To compensate, the atmosphere during these steps may contain a moderate overpressure of selenium. In the preferred embodiment, the film is selenized at a rate of 5–100 Å/s during cool-down from PVD temperature to annealing temperature.

Once the CIGS layers 18 and 20 collectively are deposited and annealed, a thin layer 22 of n-type semiconductor comprising cadmium sulfide is deposited next. CdS layer 22 is preferably deposited by chemical bath deposition (CBD) to a thickness of approximately 200–1000 Å. The CBD bath may be prepared from 0.08 gm CdSO₄, 2.5 gm thiourea, and 27.5 gm NH₄OH dissolved in 200 ml water. The deposition temperature should be approximately 40°–80° C.

A layer 28 of conducting wide bandgap n-type semiconductor materials is deposited next. In the preferred embodiment, layer 28 comprises two zinc oxide layers 24 and 26 as shown in FIG. 2. First zinc oxide layer 24 is deposited with RF sputtering at approximately 0.62 watts/cm² in an argon plasma at 10 millitorrs pressure. Second zinc oxide layer 26, comprising approximately 1–5% Al₂O₃-doped zinc oxide, is also prepared using RF sputtering at approximately 1.45 watts/cm² in an argon plasma at 10 millitorrs pressure. In an exemplary embodiment the resistivity of the first layer was 50–200 ohm/cm², and resistivity of the second layer was 15–20 ohm/cm². The transmissivity of the overall ZnO layer was 80–85%.

Bi-layer metal contacts 30 may then be prepared with an e-beam system or other techniques. In an exemplary embodiment a first metal contact layer was 500–1000 Å thick Ni and the second metal contact layer was 1–3 μm thick Al. Metal contacts 30 will generally be laid out in fine grid lines across the collecting surface of the device and connected to a suitable current collecting electrode (not shown). The efficiency of the resulting device can be further increased by adding an antireflection coating 32, such as a 600–1000 Å layer of MgF₂ by electron beam. A device prepared according to Example 3 below exhibited a conversion efficiency of 9.44%.

EXAMPLE 1

A photovoltaic precursor film of In₁₋₂Se₁₋₃ was electrodeposited on glass substrates coated with a Mo or Mo/Cu layer approximately 500 Å thick. The precursor film was deposited using an electroplating solution containing 2.25 gm InCl₃ and 0.41 gm H₂SeO₃ dissolved in 200 ml of water. The pH of the solution was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume) with an alternating current voltage of 0.45 V at 18.1 KHz frequency. The films were 1–3 μm thick and adhered to the substrate.

EXAMPLE 2

A photovoltaic precursor film of Cu₁₋₂Se₁₋₃ was electrodeposited on a substrate using an electroplating solution containing 6.21 gm Cu(NO₃)₂·6H₂O and 1.16 gm H₂SeO₃ dissolved in 300 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate.

EXAMPLE 3

A photovoltaic precursor film of Cu₁₋₂In₁₋₂Se₁₋₃ was electrodeposited on a substrate using an electroplating solution containing 4.47 gm CuCl₂, 5.67 gm InCl₃ and 3.39 gm H₂SeO₃ dissolved in 1050 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate. The electrodeposited film was slightly indium poor. Indium was then added by vapor deposition to adjust the final content to approximately CuInSe₂. CdS and ZnO were then added to complete the solar cell. The resulting solar cell was exposed to ASTM E892-87 Global (1000 Wm⁻²) standard irradiance spectrum at 25° C. Performance parameters for the finished solar cell, having an area of 0.4285 cm², were measured as:

$V_{oc} = 0.4138 \text{ V}$	$V_{pmax} = 0.3121 \text{ V}$
$I_{sc} = 15.40 \text{ mA}$	$I_{pmax} = 12.96 \text{ mA}$
$J_{sc} = 35.94 \text{ mA cm}^{-2}$	$P_{max} = 4.045 \text{ mW}$
Fill Factor = 63.47%	Efficiency = 9.44%

FIG. 3 is an I-V plot for the device. FIG. 4 is a plot of the relative quantum efficiency of the device. The device contained only Cu—In—Se, without any gallium. The device exhibited an efficiency of 8.76% without antireflective coating, and 9.44% after an antireflective coating was added. It is believed that by adding gallium the efficiency of the resulting cell could be improved to around fourteen percent (14%).

EXAMPLE 4

A photovoltaic precursor film of Cu₁₋₂In₁₋₂Ga_{0.01-1}Se₁₋₃ was electrodeposited using a solution containing 1.12 gm Cu(NO₃)₂·6H₂O, 12.0 gm InCl₃, 4.60 gm Ga(NO₃)₃·xH₂O and 1.80 gm H₂SeO₃ dissolved in 450 ml of water. This is equivalent to approximately 2.49 gm/l Cu(NO₃)₂·6H₂O, 26.7 gm/l InCl₃, 10.2 gm/l Ga(NO₃)₃·xH₂O and 4.0 gm/l H₂SeO₃, and approximately 0.0084, 0.12, 0.28, and 0.31 molar of copper, indium, gallium, and selenium ions, respectively. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate.

EXAMPLE 5

A photovoltaic precursor film of Cu₁₋₂In₁₋₂Ga_{0.01-1}Se₁₋₃ was electrodeposited using a solution containing 1.496 gm Cu(NO₃)₂·5H₂O, 14.929 gm InCl₃, 1.523 gm H₂SeO₃, and 7.192 gm Ga(NO₃)₃ dissolved in 450 ml of DMSO. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

EXAMPLE 6

A photovoltaic precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , and 7.192 gm $\text{Ga}(\text{NO}_3)_3$ dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

EXAMPLE 7

A photovoltaic precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , 7.192 gm $\text{Ga}(\text{NO}_3)_3$, and 10 gm Na_2SO_4 , and 20 gm LiCl dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

The present invention as described above may be incorporated in a variety of applications, as for example the conversion of solar energy to electric energy for baseline power generation. Other applications include appliances such as solar-powered calculators, battery charges such as those used with freeway emergency call boxes, photoelectric eyes, night security light activators, light meters for photographic and other purposes, and the like.

Although the present invention has thus been described in detail with regard to the preferred embodiments and drawings and examples thereof, it should be apparent to those skilled in the art that various adaptations and modifications of the present invention may be accomplished without departing from the spirit and the scope of the invention. Accordingly, it is to be understood that the detailed description and the accompanying drawings as set forth hereinabove are not intended to limit the breadth of the present invention, which should be inferred only from the following claims and their appropriately construed legal equivalents.

What is claimed is:

1. A process for preparing a metal-containing thin film, the process comprising the steps of:

electrodepositing a layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) on a substrate, the electrodeposition proceeding at a DC voltage of approximately 1-10 V and an AC voltage of approximately 0.2-5.0 V at 1-100 KHz superimposed upon said DC voltage; and

depositing a sufficient amount of either In+Se or Cu+Se on said layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ by vapor deposition to produce a thin film of $\text{Cu}(\text{In,Ga})\text{Se}_2$ on the substrate wherein said thin film has stoichiometric ratios of approximately $\text{Cu}=1-1.2$; $(\text{In,Ga})=1-1.2$; $\text{Se}=2-2.5$.

2. The process of claim 1 wherein said layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) comprises $\text{In}_{1-2}\text{Se}_{1-3}$.

3. The process of claim 1 wherein said layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) comprises $\text{Cu}_{1-2}\text{Se}_{1-3}$.

4. The process of claim 1 wherein said layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) comprises $\text{Cu}_{1-2}\text{In}_{1-2}\text{Se}_{1-3}$.

5. The process of claim 1 wherein said layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) comprises $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ ($x=1-2$, $y=1-2$, $z=0.01-1$, $n=1-3$).

6. The process of claim 1 wherein the vapor deposition comprises physical vapor deposition.

7. The process of claim 6 wherein the physical vapor deposition proceeds at a temperature of approximately 550° C.

8. The process of claim 1 wherein the electrodeposition proceeds in an aqueous electrodeposition solution, said DC voltage is approximately 1-5 volts, and said AC voltage is approximately 0.3-1.0 volts at approximately 10-30 KHz.

9. The process of claim 8 wherein said DC voltage is approximately 2 volts and said AC voltage is approximately 0.45 volts at approximately 18.1 KHz.

10. The process of claim 1 wherein said DC voltage is approximately 3-10 volts, and the electrodeposition proceeds in an electrodeposition solution comprising at least one organic solvent, and the electrodeposition further proceeds at an AC voltage of approximately 0.2-5.0 volts at approximately 1-100 KHz superimposed upon said DC voltage.

11. The process of claim 10 wherein said AC voltage is approximately 0.45 volts at approximately 18.1 KHz.

12. The process of claim 1 wherein the electrodeposition step proceeds in an electrodeposition solution comprising at least one supporting electrolyte for raising the conductivity of the electrodeposition solution and increasing the deposition rate of the $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ layer.

13. The process of claim 12 wherein said supporting electrolyte comprises at least one compound selected from the group consisting of NaCl, LiCl, and Na_2SO_4 .

14. The process of claim 1 further comprising the steps of: depositing a CdS layer on the $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ film by chemical bath deposition; and

depositing a ZnO layer on the CdS layer by RF sputtering.

15. A process for preparing a solar cell precursor thin film, the process comprising the steps of:

(a) providing an electrodeposition solution containing copper, indium, gallium, and selenium ions;

(b) immersing a substrate into said electrodeposition solution; and

(c) electroplating said copper, indium, gallium, and selenium ions simultaneously onto said substrate by applying a cathodic potential thereto of 1-10 VDC voltage and 0.2-5.0 VAC at 1-100 KHz superimposed thereon.

16. The process according to claim 15, wherein said electrodeposition solution includes at least one organic solvent.

17. The process according to claim 16, wherein said cathodic potential is approximately 2 VDC and approximately 0.45 VAC at 10-30 KHz superimposed thereon.

18. The process according to claim 15, wherein said cathodic potential is approximately 1-5 VDC and 0.3-1.0 VAC at 10-30 KHz superimposed thereon.

19. The process according to claim 18, wherein said electrodeposition solution comprises approximately 2.49 gm/l $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 26.7 gm/l InCl_3 , 10.2 gm/l $\text{Ga}(\text{NO}_3)_3$, and 4.0 gm/l H_2SeO_3 .

20. The process according to claim 19, wherein said electrodeposition solution includes at least one organic solvent.

* * * * *



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United States Patent [19]**Bhattacharya et al.**[11] **Patent Number:** **5,804,054**[45] **Date of Patent:** **Sep. 8, 1998**[54] **PREPARATION OF COPPER INDIUM
GALLIUM DISELENIDE FILMS FOR SOLAR
CELLS**

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[73] Assignee: **Davis, Joseph & Negley**, Austin, Tex.[21] Appl. No.: **979,358**[22] Filed: **Nov. 26, 1997****Related U.S. Application Data**

[62] Division of Ser. No. 571,150, Dec. 12, 1995, Pat. No. 5,730,852.

[60] Provisional application No. 60/004,269, Sep. 25, 1995.

[51] Int. Cl.⁶ **H01L 31/18; C25D 3/56**[52] U.S. Cl. **205/239; 205/103; 205/915;
 136/264; 136/265; 437/5**[58] Field of Search **205/239, 103,
 205/915; 136/264, 265; 437/5**[56] **References Cited****U.S. PATENT DOCUMENTS**

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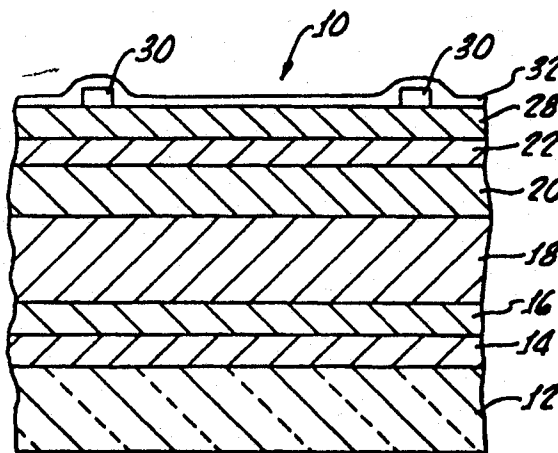
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Primary Examiner—Kathryn L. Gorgos*Assistant Examiner*—Kishor Mayekar*Attorney, Agent, or Firm*—Joel D. Voelzke; Oppenheimer Wolff & Donnelly LLP[57] **ABSTRACT**

High quality thin films of copper-indium-gallium-diselenide useful in the production of solar cells are prepared by electrodepositing at least one of the constituent metals onto a glass/Mo substrate, followed by physical vapor deposition of copper and selenium or indium and selenium to adjust the final stoichiometry of the thin film to approximately Cu(In, Ga)Se₂. Using an AC voltage of 1-100 KHz in combination with a DC voltage for electrodeposition improves the morphology and growth rate of the deposited thin film. An electrodeposition solution comprising at least in part an organic solvent may be used in conjunction with an increased cathodic potential to increase the gallium content of the electrodeposited thin film.

8 Claims, 2 Drawing Sheets

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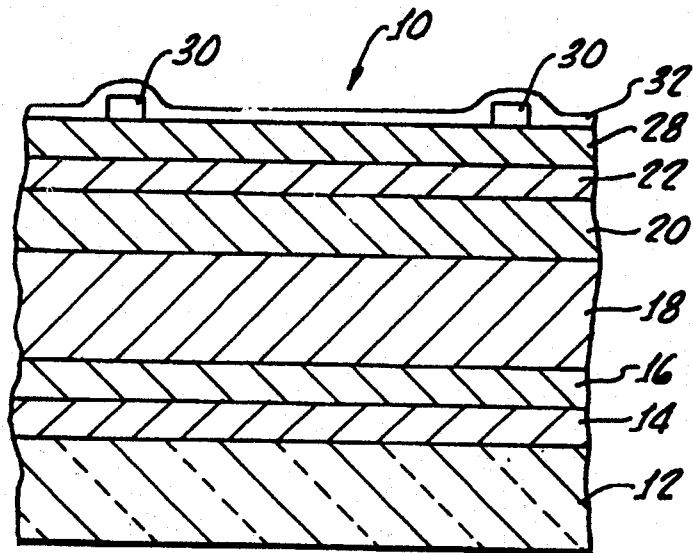


FIG. 1.

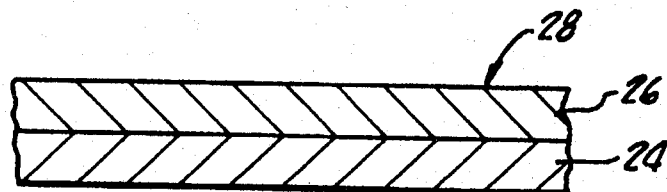
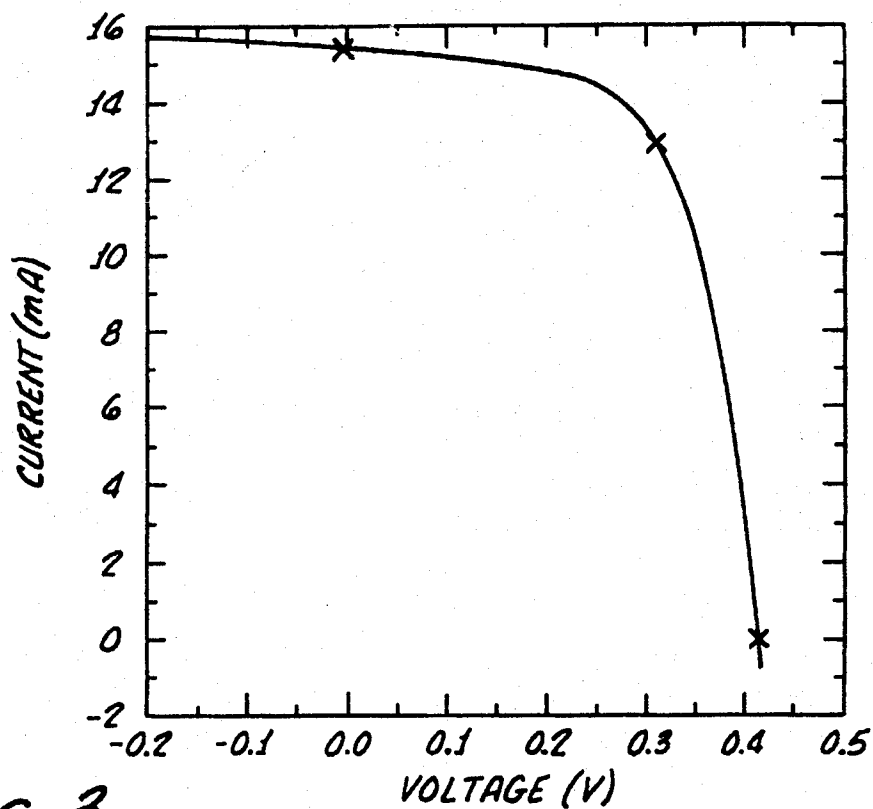
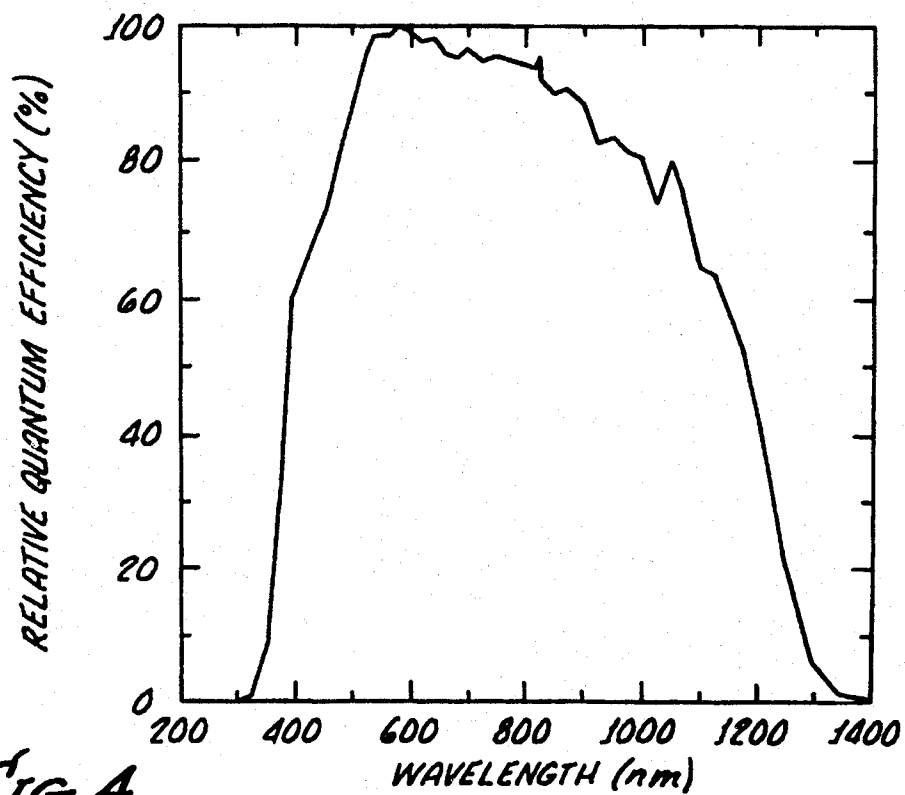


FIG. 2.

FIG. 3.FIG. 4.

PREPARATION OF COPPER INDIUM GALLIUM DISELENIDE FILMS FOR SOLAR CELLS

RELATED APPLICATIONS

This application is a divisional of U.S. application Ser. No. 08/571,150, filed Dec. 12, 1995, now U.S. Pat. No. 5,730,852 which is a continuation-in-part of provisional application Ser. No. 60/004,269, filed Sep. 25, 1995.

The government has rights in this invention pursuant to National Renewable Energy Laboratory (NREL) contract No. 1326.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of the present invention relates to the preparation of thin film semiconductor devices. More particularly, the present invention relates to electrodeposition of copper-indium-gallium-selenide films for solar cells.

2. Description of the Related Art

Chalcopyrite ternary thin films of copper-indium-diselenide (CuInSe_2) and copper-indium-gallium-diselenide ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$), both of which are generically referred to as Cu(In,Ga)Se_2 , CIGS, or simply CIS, have become the subject of considerable interest and study for semiconductor devices in recent years. Sulphur can also be, and sometimes is, substituted for selenium, so the compound is sometimes also referred to even more generically as Cu(In,Ga)(Se,S)_2 so as to encompass all of these possible combinations. These devices are also referred to as I-III-VI₂ devices according to their constituent elemental groups.

These devices are of particular interest for photovoltaic device or solar cell absorber applications. For photovoltaic applications, the p-type CIGS layer is combined with an n-type CdS layer to form a p-n heterojunction CdS/CIGS device. The direct energy gap of CIGS results in a large optical absorption coefficient, which in turn permits the use of thin layers on the order of 1–2 μm . An additional advantage of CIGS devices is their long-term stability.

Various methods have been reported for fabricating CIGS thin films. Some of the earliest techniques involved heating copper and indium on a substrate in the presence of a selenium-containing gas, including H_2Se . The heating of copper and indium films in the presence of a selenium-containing gas is known as selenization. One drawback to selenizing with H_2Se is that H_2Se gas is highly toxic, thus presenting serious hazards to humans in large scale production environments.

In U.S. Pat. No. 5,045,409, Eberspacher et al. disclose depositing copper and indium films by magnetron sputtering, and depositing a selenium film by thermal evaporation, followed by heating in the presence of various gases. Other methods for producing CIS films have included Molecular Beam Epitaxy, electrodeposition either in single or multiple steps, and vapor deposition of single crystal and polycrystalline films.

Although vapor deposition techniques have been used to yield solar cells with efficiencies as high as seventeen percent (17%), vapor deposition is costly. Accordingly, solar cells made by vapor deposition have generally been limited to devices for laboratory experimentation, and are not suitable for large scale production. On the other hand, thin film solar cells made by electrodeposition techniques are generally much less expensive. However, solar cells produced by electrodeposition generally suffer from low efficiencies. For

example, in *Solar Cells with Improved Efficiency Based on Electrodeposited Copper Indium Diselenide Thin Films*, ADVANCED MATERIALS, Vol. 6 No. 5 (1994), Guillemoles et al. report solar cells prepared by electrodeposition with efficiencies on the order of 5.6%.

SUMMARY OF THE INVENTION

Accordingly, it is a general object of this invention to provide an improved process for fabricating high quality thin film Cu(In,Ga)Se_2 solar cells.

It is also an object of this invention to provide low cost, high quality thin film solar cells having high conversion efficiencies.

It is a further object of this invention to provide a process for producing Cu—In , Cu—Se , Cu—In—Se , and Cu—In—Ga—Se thin films that have applications in solar and non-solar cells.

It is a still further object of this invention to provide a process for electrodepositing a gallium-containing thin-film solar cell precursor.

To achieve the foregoing and other objects and advantages in accordance with the purpose of the present invention, as embodied and broadly described herein, the process of this invention includes electrodepositing a layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$), preferably using direct current in combination with alternating current, followed by vapor depositing additional copper and selenium or indium and selenium to adjust the final composition very close to stoichiometric Cu(In,Ga)Se_2 . This unique two-step film deposition process allows precursor films to be deposited by inexpensive electrodeposition, and then adjusted using the more expensive but more precise technique of physical vapor deposition to bring the final film into the desired stoichiometric range. Solar cells may then be completed as for example by chemical bath deposition (CBD) of CdS followed by sputtering of ZnO, and addition of bi-layer metal contacts as well as optional anti-reflective coating. A solar cell made according to the present process has exhibited a device efficiency of 9.44%.

Additional objects, advantages, and novel features of the present invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a CIGS photovoltaic device prepared according to the present invention.

FIG. 2 is a cross sectional view of the conducting zinc oxide layer 28 shown in FIG. 1.

FIG. 3 is the current vs. voltage performance plot of a CdS/ CuInSe_2 solar cell prepared according to Example 3 of the present invention.

FIG. 4 is a plot of relative quantum efficiency verses wavelength for the CdS/ CuInSe_2 solar cell of Example 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention includes an essentially two-step process for fabricating high quality, low cost thin film CIGS semiconductor devices that exhibit photovoltaic characteristics and are especially adaptable for solar cell applications. In the first step, a precursor film of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) is electrodeposited on a substrate

such as glass coated with molybdenum. This first step may include a unique process and electrodeposition bath for electrodepositing gallium concurrently with other elements, as well as the unique use of an alternating current in conjunction with a direct current.

The second step is physical vapor deposition of either Cu+Se or In+Se, either alone or in combination with Ga. In this second step the composition of the overall film is carefully controlled so that the resulting thin film is very close to stoichiometric Cu(In,Ga)Se_2 . Both of these steps may be performed on substrates having large surface areas. Accordingly, the process of the present invention allows large area, high efficiency solar cells to be economically produced.

Referring now to FIG. 1, CdS/CIGS photovoltaic device 10 includes a substrate 12 which may be, for example, soda-lime silica glass or amorphous 7059 glass. Substrate 12 further includes a back contact layer 14 of molybdenum, about 1–2 μm thick. The molybdenum may be deposited using DC sputtering from a rotating cylindrical magnetron target (CMAG). To improve adhesion between the Mo layer 14 and the precursor film to be deposited, an additional adhesion layer 16 of copper may also be deposited as by electrodeposition. After Mo layer 14 and optional copper adhesion layer 16 have been deposited, the substrate should be degreased as for example with propanol and dried in flowing nitrogen gas.

A precursor film 18 is then deposited by electrodeposition. The precursor film contains one or more of the elements copper, indium, gallium, and selenium. Electrodeposition is generally a less expensive method of depositing these materials than vapor deposition. However, it is not possible to control the ratios of metals deposited during electrodeposition as precisely as desired. Consequently, prior CIGS layers deposited entirely by electrodeposition produced low conversion efficiencies. In the present invention, the electrodeposition step is integrated with the vapor deposition step that follows. This allows precursor material to be deposited in bulk using an economical electrodeposition step, followed by a vapor deposition step to carefully control the final elemental ratios. This results in economical production yet high efficiencies of the resulting cell. The composition of precursor film 18 is generally denoted as $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$). The precursor film 18 should be deposited to about 1–3 μm thick, with thickness being controlled by coulometric measurements.

It has been found that electrodepositing the films using an AC voltage in addition to a DC voltage produces improved results. An AC voltage improves the morphology of the film. It is also believed that the AC voltage improves nucleation (growth) of the thin film by allowing additional nucleation centers to be created. For an entirely aqueous plating solution, the applicable DC voltage range is approximately 1–5 VDC, with a preferred voltage of approximately 2 VDC. Improved results may be obtained by superimposing an AC voltage of 0.2–5.0 VAC at 1–100 KHz, with preferred values of approximately 0.3–1.0 VAC at 10–30 KHz. A value of approximately 0.45 VAC at approximately 18.1 KHz was found to yield good results. The plating solution is adjusted to have a pH of approximately 1.0 to 4.0, and more preferably to about 1.4 to 2.4. The plating solution should preferably be at about 10° C. to 80° C., and more preferably at about 24° C. Adding a supporting electrolyte to the plating bath can additionally increase the conductivity of the plating solution, allowing for a further increase in the electrodeposition rate. Salts such as NaCl, LiCl, or Na_2SO_4 have been found to be suitable supporting electrolytes for use with certain embodiments of the present invention.

In completely aqueous solutions, electrolysis of water molecules begins to occur to an undesirable extent at approximately 2–3 volts. The resulting O^{2-} and OH^- ions combine with deposition metal ions or deposited metal to form unwanted metal oxides and hydroxides on the precursor film 18. To overcome this disadvantage, the water in the plating solution may be either partially or completely replaced by one or more organic solvents such as dimethyl sulfoxide (DMSO). Increasing the organic solvent content of the electrodeposition solution allows the cathodic potential to be increased without unacceptable increases in metal oxide and hydroxide formation rates. The increased cathodic potential increases the deposition rate of the precursor films. An additional advantage is that increasing the cathodic potential increases the deposition rate of gallium relative to the deposition rates of other deposited metals. Therefore, using a solution containing one or more organic solvents allows the cathodic potential to be selected from a wider range so as to achieve a more desired stoichiometry of the as-deposited precursor film 18. When an organic solvent is used, the preferred cathodic potential is approximately 3–10 VDC and 0.2–5.0 VAC at approximately 1–100 KHz. Value of approximately 5 VDC and 0.45 VAC at approximately 18.1 KHz were found to yield good results.

If desired, a second electroplating solution may be employed to adjust the stoichiometry of the electrodeposited film prior to the vapor deposition phase. For example, a first electrodeposition step may produce a CIGS precursor film with less gallium than optimally desired. Although the gallium content can be increased during the vapor deposition phase, it may be less expensive to deposit a certain amount of gallium using a second electrodeposition solution to make a coarse stoichiometric adjustment prior to proceeding to fine stoichiometric adjustment at the vapor deposition step. Another potential motivation for using a second electrodeposition solution is to achieve a composition gradient in the deposited film, as suggested by U.S. Pat. No. 4,335, 266 issued to Michelsen et al. which is hereby incorporated by reference for its teachings of composition-graded CIGS thin films for solar cell and other applications. Yet another way of achieving composition grading during electrodeposition is to vary process parameters such as cathodic potential, ionic concentrations, pH, or temperature, as electrodeposition proceeds.

Several examples of electrodeposited precursor films fabricated according to the present invention are given. These examples include In—Se, Cu—Se, and Cu—In—Se precursor films. For these precursor films, Ga should be added to raise the energy gap. The Ga may be added by a separate electrodeposition step, though is preferably added at the vapor deposition step by vaporizing elemental gallium. An example is also given of a novel solution and process that allows Ga to be electrodeposited along with other precursor metals, to produce a Cu—In—Ga—Se precursor film electrodeposited in a single step. The solution includes ions of each of the elements of copper, indium, gallium, and selenium. These ions may be supplied in the form of dissolved metal salts.

After the precursor film 18 has been electrodeposited it should be cleaned. A suitable method is to rinse precursor film 18 with deionized water and dry it in flowing nitrogen gas. After precursor film 18 has been cleaned, an additional layer 20 of In+Se or Cu+Se, either alone or in combination with gallium, is deposited by physical vapor deposition to adjust the final film composition to the ratios of approximately $\text{Cu}=1-1.2$, $(\text{In,Ga})=1-1.2$, $\text{Se}=2-2.5$, and most preferably to approximately 1:1:2. By controlling the ratio of

In/Ga the energy gap between the CdS and the CIGS layers can be adjusted to the optimal or nearly optimal value. An energy gap of approximately 1.45 eV is considered optimal for terrestrial solar energy conversion, and is achieved by an In/Ga ratio of approximately 3:1. The substrate (precursor film) temperature should be 300° C. to 600° C. during PVD, and preferably about 550° C.

After PVD, the films should then be annealed. Annealing improves the homogeneity and quality of the films. A high quality CIGS film is one that does not exhibit an excessive amount of copper nodules, voids, or vacancies in the film which would reduce conversion efficiencies. Annealing the films at 250° C. to 500° C. in a vacuum, followed by slow cooling at a rate of approximately 3° C./min to avoid thermal shock was found to yield good results. Because selenium has a much higher vapor pressure than either copper, indium, or gallium, selenium may be lost from the film during the high temperature steps of vapor deposition and annealing. To compensate, the atmosphere during these steps may contain a moderate overpressure of selenium. In the preferred embodiment, the film is selenized at a rate of 5–100 Å/s during cool-down from PVD temperature to annealing temperature.

Once the CIGS layers 18 and 20 collectively are deposited and annealed, a thin layer 22 of n-type semiconductor comprising cadmium sulfide is deposited next. CdS layer 22 is preferably deposited by chemical bath deposition (CBD) to a thickness of approximately 200–1000 Å. The CBD bath may be prepared from 0.08 gm CdSO₄, 2.5 gm thiourea, and 27.5 gm NH₄OH dissolved in 200 ml water. The deposition temperature should be approximately 40°–80° C.

A layer 28 of conducting wide bandgap n-type semiconductor materials is deposited next. In the preferred embodiment, layer 28 comprises two zinc oxide layers 24 and 26 as shown in FIG. 2. First zinc oxide layer 24 is deposited with RF sputtering at approximately 0.62 watts/cm² in an argon plasma at 10 millitorrs pressure. Second zinc oxide layer 26, comprising approximately 1–5% Al₂O₃-doped zinc oxide, is also prepared using RF sputtering at approximately 1.45 watts/cm² in an argon plasma at 10 millitorrs pressure. In an exemplary embodiment the resistivity of the first layer was 50–200 ohm/cm², and resistivity of the second layer was 15–20 ohm/cm². The transmissivity of the overall ZnO layer was 80–85%.

Bi-layer metal contacts 30 may then be prepared with an e-beam system or other techniques. In an exemplary embodiment a first metal contact layer was 500–1000 Å thick Ni and the second metal contact layer was 1–3 μm thick Al. Metal contacts 30 will generally be laid out in fine grid lines across the collecting surface of the device and connected to a suitable current collecting electrode (not shown). The efficiency of the resulting device can be further increased by adding an antireflection coating 32, such as a 600–1000 Å layer of MgF₂ by electron beam. A device prepared according to Example 3 below exhibited a conversion efficiency of 9.44%.

EXAMPLE 1

A precursor film of In_{1.2}Se_{1.3} was electrodeposited on glass substrates coated with a Mo or Mo/Cu layer approximately 500 Å thick. The precursor film was deposited using an electroplating solution containing 2.25 gm InCl₃ and 0.41 gm H₂SeO₃ dissolved in 200 ml of water. The pH of the solution was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alter-

nating current voltage of 0.45 V at 18.1 KHz frequency. The films were 1–3 μm thick and adhered to the substrate.

EXAMPLE 2

A precursor film of Cu_{1.2}Se_{1.3} was electrodeposited on a substrate using an electroplating solution containing 6.21 gm Cu(NO₃)₂·6H₂O and 1.16 gm H₂SeO₃ dissolved in 300 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate.

EXAMPLE 3

A precursor film of Cu_{1.2}In_{1.2}Se_{1.3} was electrodeposited on a substrate using an electroplating solution containing 4.47 gm CuCl₂, 5.67 gm InCl₃ and 3.39 gm H₂SeSO₃ dissolved in 1050 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate. The electrodeposited film was slightly indium poor. Indium was then added by vapor deposition to adjust the final content to approximately CuInSe₂. CdS and ZnO were then added to complete the solar cell. The resulting solar cell was exposed to ASTM E892-87 Global (1000 Wm⁻²) standard irradiance spectrum at 25° C. Performance parameters for the finished solar cell, having an area of 0.4285 cm², were measured as:

$V_{oc} = 0.4138 \text{ V}$	$V_{Pmax} = 0.3121 \text{ V}$
$I_{sc} = 15.40 \text{ mA}$	$I_{Pmax} = 12.96 \text{ mA}$
$J_{sc} = 35.94 \text{ mA cm}^{-2}$	$P_{max} = 4.045 \text{ mW}$
Fill Factor = 63.47%	Efficiency = 9.44%

FIG. 3 is an I-V plot for the device. FIG. 4 is a plot of the relative quantum efficiency of the device. The device contained only Cu—In—Se, without any gallium. The device exhibited an efficiency of 8.76% without antireflective coating, and 9.44% after an antireflective coating was added. It is believed that by adding gallium the efficiency of the resulting cell could be improved to around fourteen percent (14%).

EXAMPLE 4

A precursor film of Cu_{1.2}In_{1.2}Ga_{0.01-1}Se_{1.3} was electrodeposited using a solution containing 1.12 gm Cu(NO₃)₂·6H₂O, 12.0 gm InCl₃, 4.60 gm Ga(NO₃)₃·xH₂O and 1.80 gm H₂SeO₃ dissolved in 450 ml of water. This is equivalent to approximately 2.49 gm/l Cu(NO₃)₂·6H₂O, 26.7 gm/l InCl₃, 10.2 gm/l Ga(NO₃)₃·xH₂O and 4.0 gm/l H₂SeO₃, and approximately 0.0084, 0.12, 0.28, and 0.31 molar of copper, indium, gallium, and selenium ions, respectively. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate.

EXAMPLE 5

A precursor film of Cu_{1.2}In_{1.2}Ga_{0.01-1}Se_{1.3} was electrodeposited using a solution containing 1.496 gm Cu(NO₃)

$\cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , and 7.192 gm $\text{Ga}(\text{NO}_3)_3$ dissolved in 450 ml of DMSO. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

EXAMPLE 6

A precursor film of $\text{Cu}_{1.2}\text{In}_{1.2}\text{Ga}_{0.01-1}\text{Se}_{1.3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)\cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , and 7.192 gm $\text{Ga}(\text{NO}_3)_3$ dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

EXAMPLE 7

A precursor film of $\text{Cu}_{1.2}\text{In}_{1.2}\text{Ga}_{0.01-1}\text{Se}_{1.3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)\cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , 7.192 gm $\text{Ga}(\text{NO}_3)_3$, and 10 gm Na_2SO_4 , and 20 gm LiCl dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

The present invention as described above may be incorporated in a variety of applications, as for example the conversion of solar energy to electric energy for baseline power generation. Other applications include appliances such as solar-powered calculators, battery charges such as those used with freeway emergency call boxes, photoelectric eyes, night security light activators, light meters for photographic and other purposes, and the like.

Although the present invention has thus been described in detail with regard to the preferred embodiments and drawings and examples thereof, it should be apparent to those skilled in the art that various adaptations and modifications of the present invention may be accomplished without departing from the spirit and the scope of the invention.

Accordingly, it is to be understood that the detailed description and the accompanying drawings as set forth hereinabove are not intended to limit the breadth of the present invention, which should be inferred only from the following claims and their appropriately construed legal equivalents.

What is claimed is:

1. A process for electrodepositing a solar cell precursor thin film, the process comprising the steps of:

electrodepositing a thin film containing copper, indium, gallium, and selenium onto a substrate, the electrodeposition proceeding in an electrodeposition solution comprising copper, indium, gallium, and selenium ions.

2. The process of claim 1, wherein said electrodeposition solution comprises copper, indium, gallium, and selenium ions at concentrations of approximately 0.0084, 0.12, 0.28, and 0.31 molar, respectively.

3. The process of claim 2, wherein said electrodeposition solution comprises approximately 2.49 gm/l $\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 26.7 gm/l InCl_3 , 10.2 gm/l $\text{Ga}(\text{NO}_3)_3$, and 4.0 gm/l (H_2SeO_3) .

4. The process of claim 1, wherein the electrodeposition solution has a pH of approximately 1.0-4.0.

5. The process of claim 1 wherein the electrodeposition proceeds at a DC voltage of 1-10 V.

6. The process of claim 5 wherein the electrodeposition proceeds at a superimposed AC voltage of approximately 0.2-5.0 V at a frequency of approximately 1-100 KHz.

7. The process of claim 6 wherein said superimposed AC voltage is approximately 0.45 VAC at a frequency of approximately 18.1 KHz.

8. The process of claim 1 wherein the electrodeposition solution further comprises at least one organic solvent, and the electrodeposition proceeds at a DC voltage of approximately 3-10 volts.

* * * * *



US005871630A

United States Patent [19]

Bhattacharya et al.

[11] Patent Number: 5,871,630

[45] Date of Patent: *Feb. 16, 1999

[54] PREPARATION OF COPPER-INDIUM-GALLIUM-DISELENIDE PRECURSOR FILMS BY ELECTRODEPOSITION FOR FABRICATING HIGH EFFICIENCY SOLAR CELLS

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[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,730,852.

[21] Appl. No.: 870,081

[22] Filed: Jun. 5, 1997

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 571,150, Dec. 12, 1995, Pat. No. 5,730,852.

[60] Provisional application No. 60/044,506 Apr. 21, 1997 and provisional application No. 60/004,269 Sep. 25, 1995.

[51] Int. Cl.⁶ C23C 28/02

[52] U.S. Cl. 205/192; 136/264; 136/265; 205/102

[58] Field of Search 205/192, 102; 437/170, 172; 136/264, 265

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Primary Examiner—Kathryn Gorgos

Assistant Examiner—Edna Wong

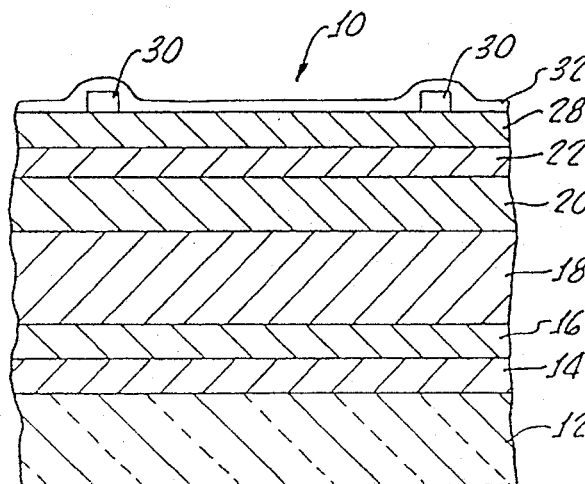
Attorney, Agent, or Firm—Oppenheimer Wolff & Donnelly LLP

[57]

ABSTRACT

A photovoltaic cell exhibiting an overall conversion efficiency of 13.6% is prepared from a copper-indium-gallium-diselenide precursor thin film. The film is fabricated by first simultaneously electrodepositing copper, indium, gallium, and selenium onto a glass/molybdenum substrate (12/14). The electrodeposition voltage is a high frequency AC voltage superimposed upon a DC voltage to improve the morphology and growth rate of the film. The electrodeposition is followed by physical vapor deposition to adjust the final stoichiometry of the thin film to approximately Cu(In_{1-x}Ga_x)Se₂, with the ratio of Ga/(In+Ga) being approximately 0.39.

16 Claims, 8 Drawing Sheets



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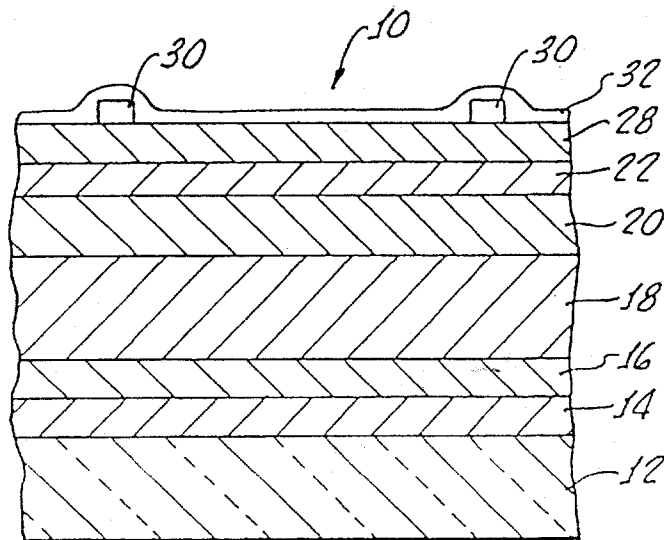


FIG. 1.

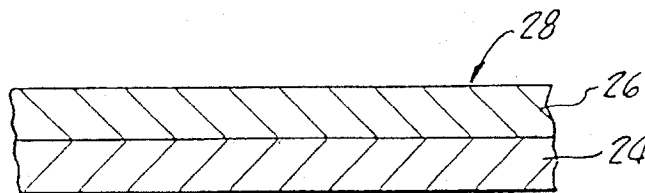
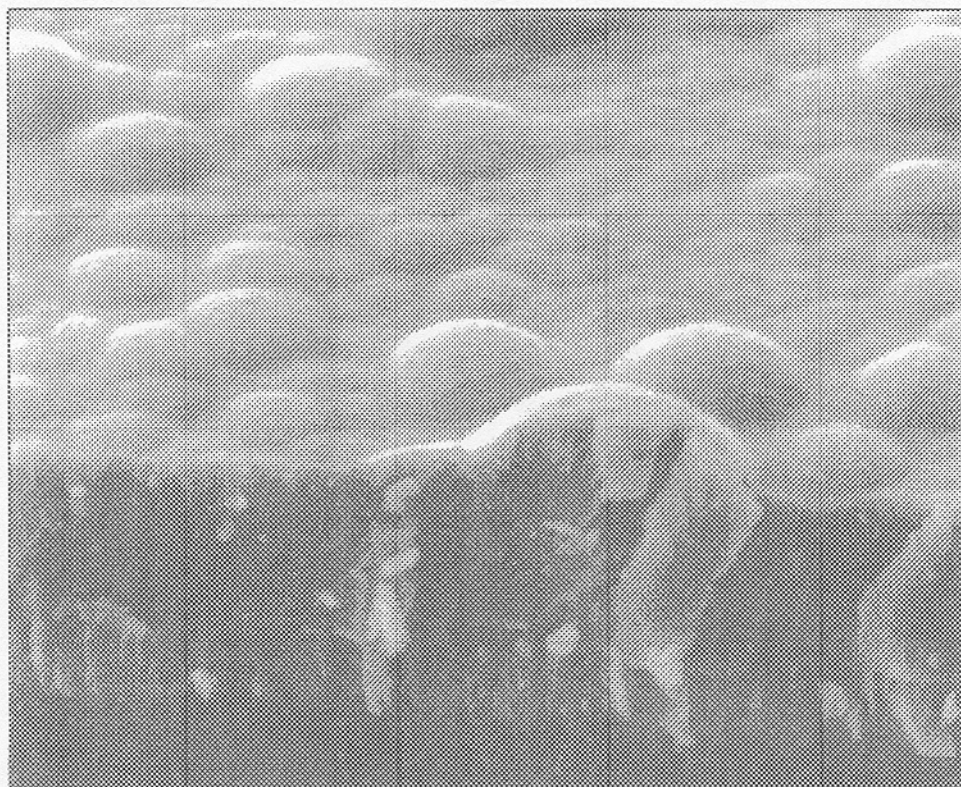


FIG. 2.

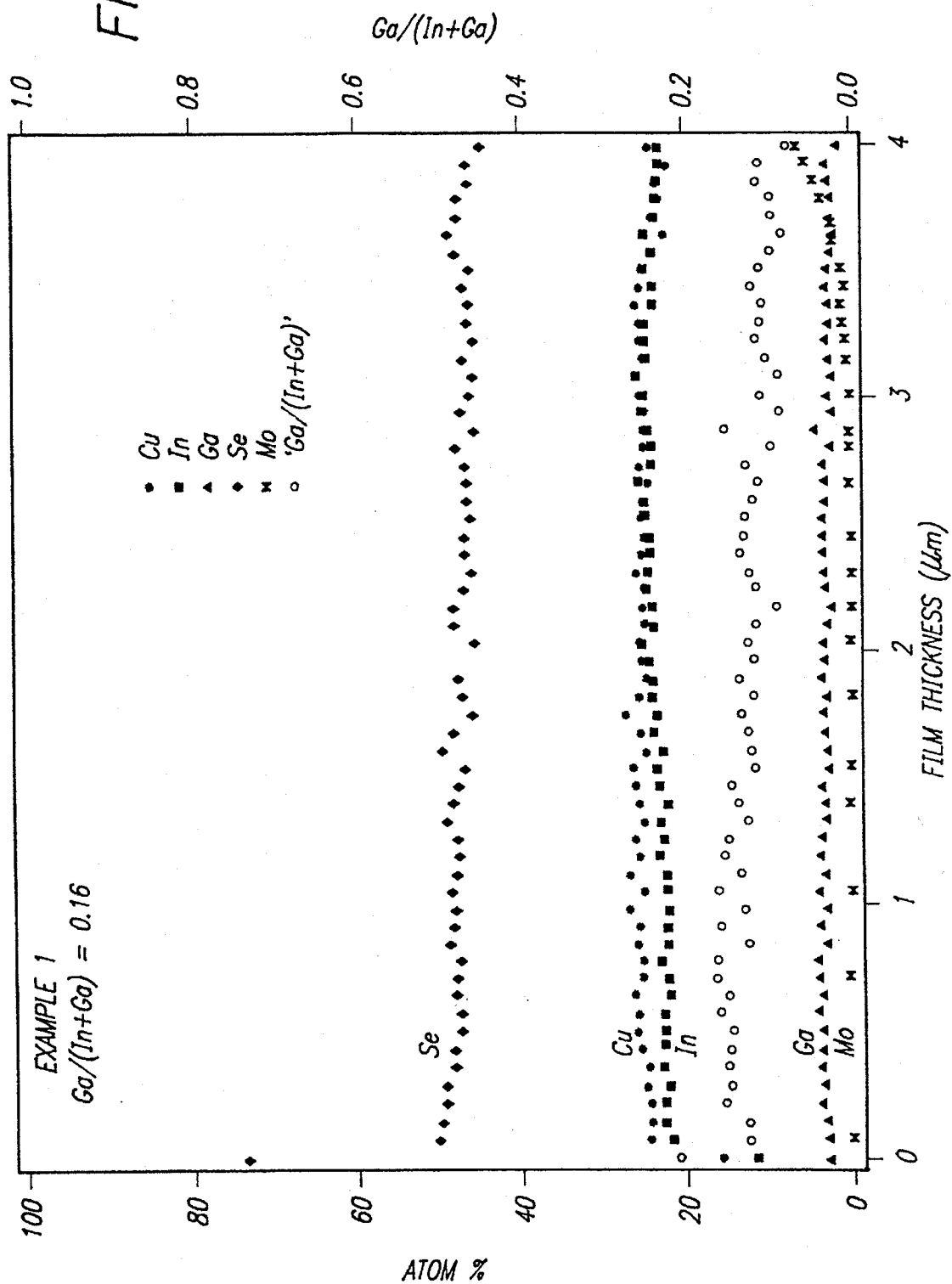
FIG. 3

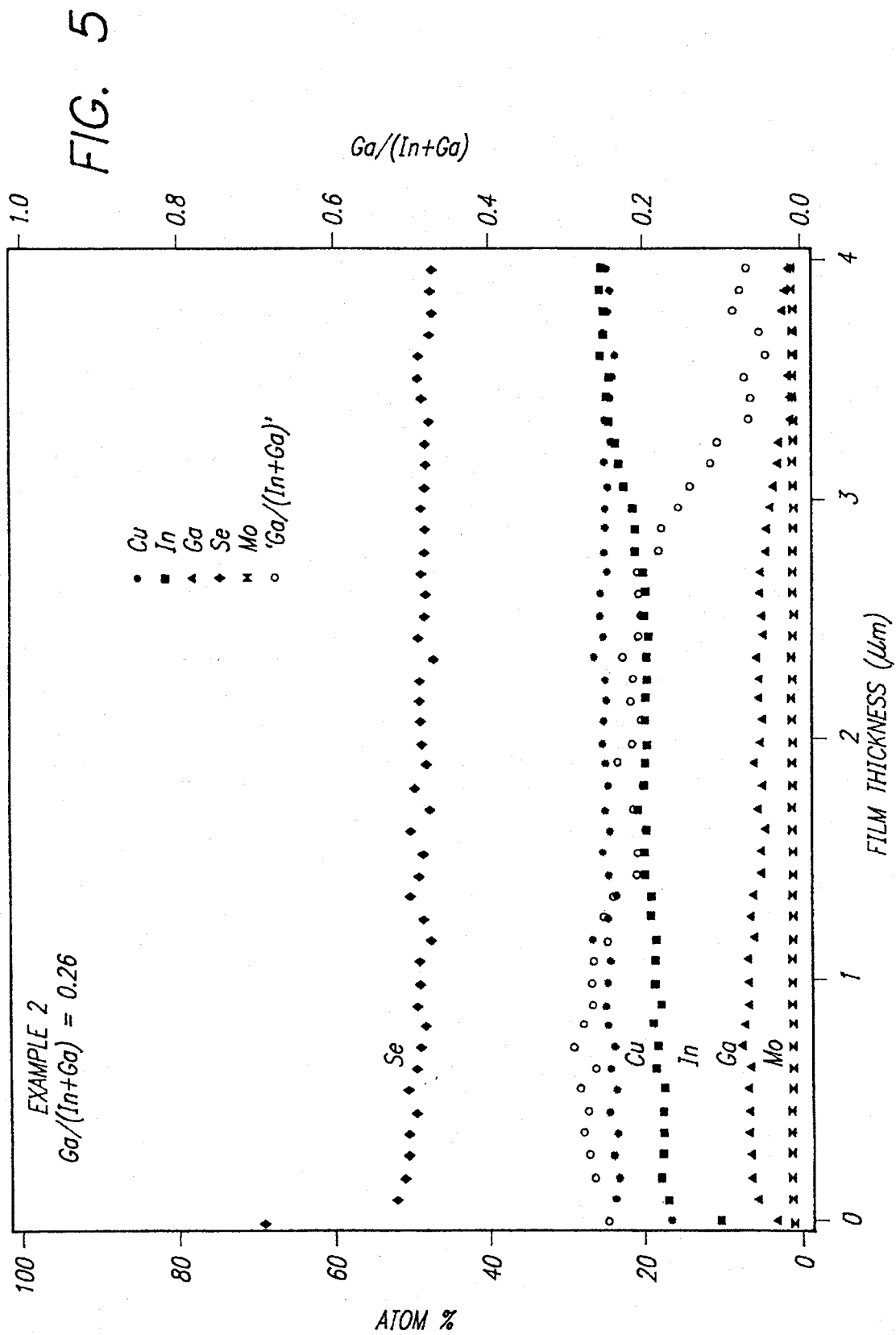


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1 μ m

FIG. 4





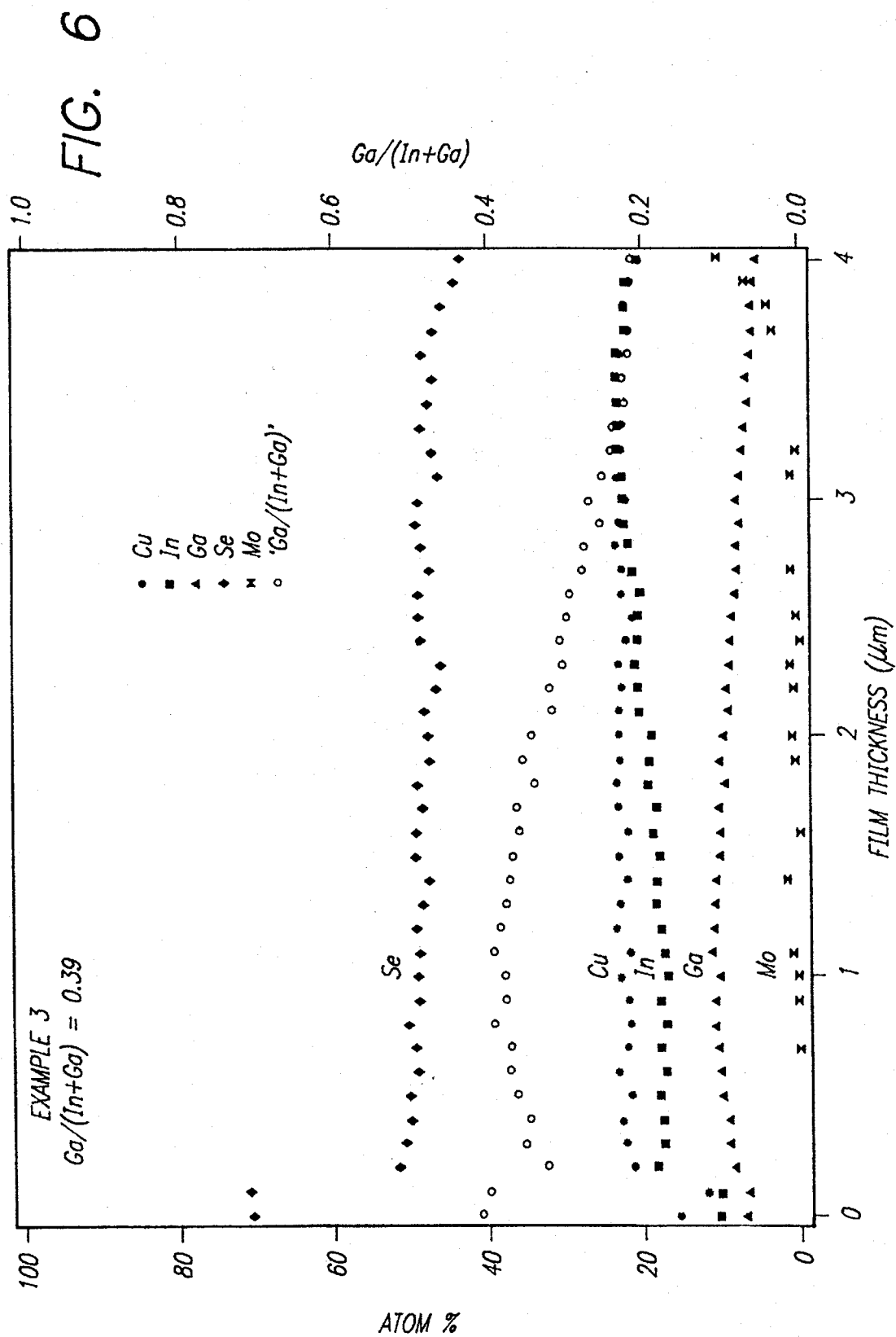
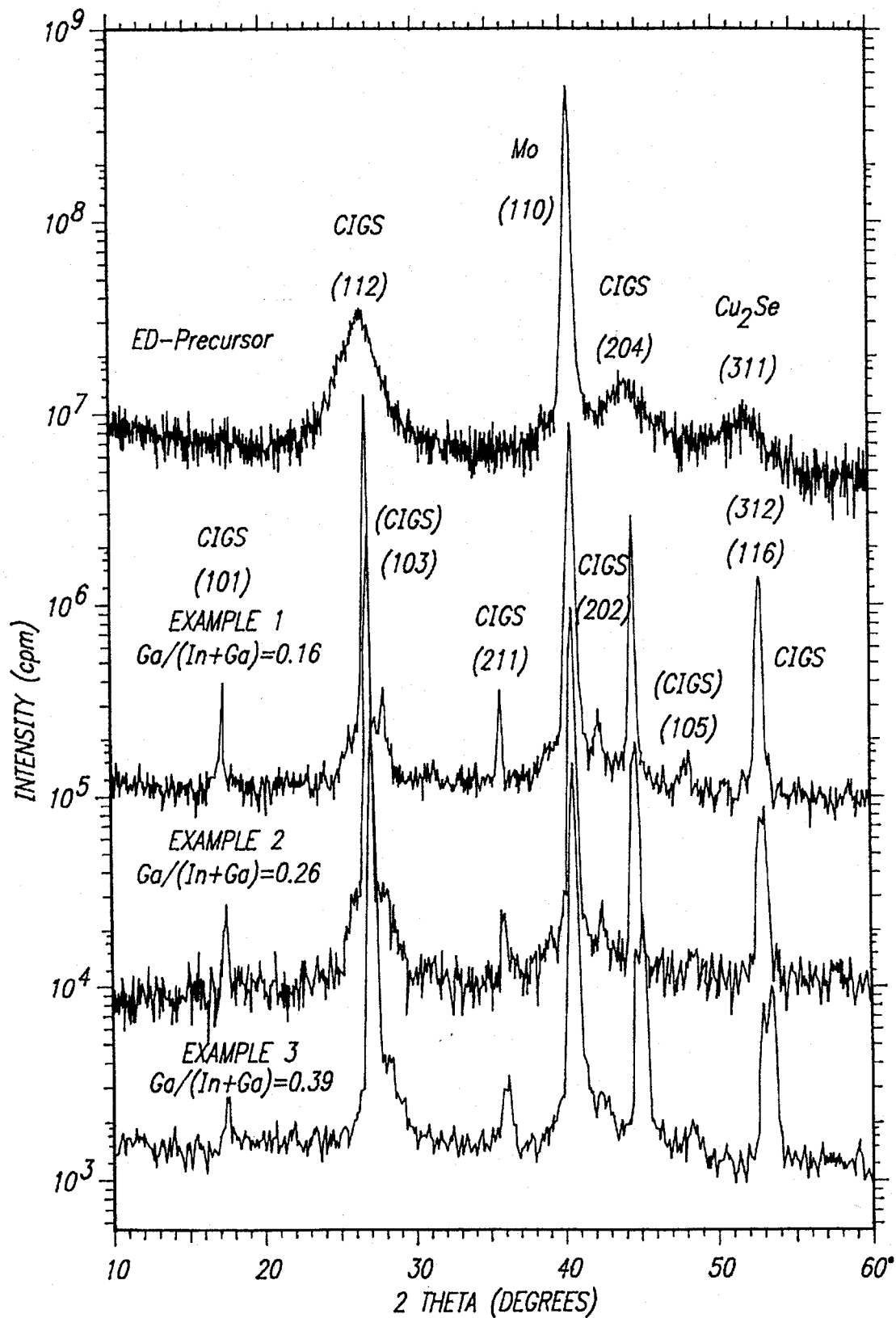


FIG. 7



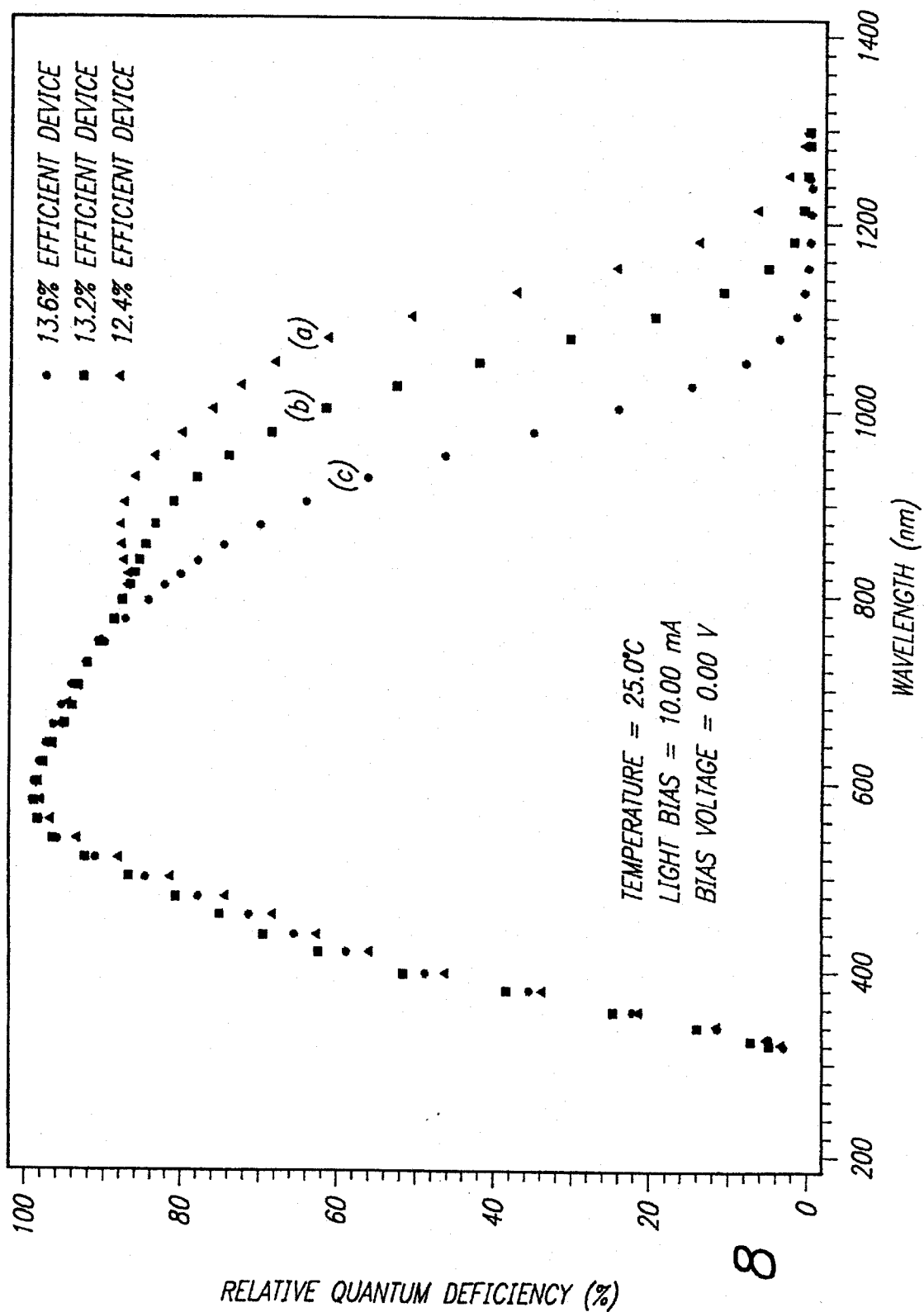


FIG. 8

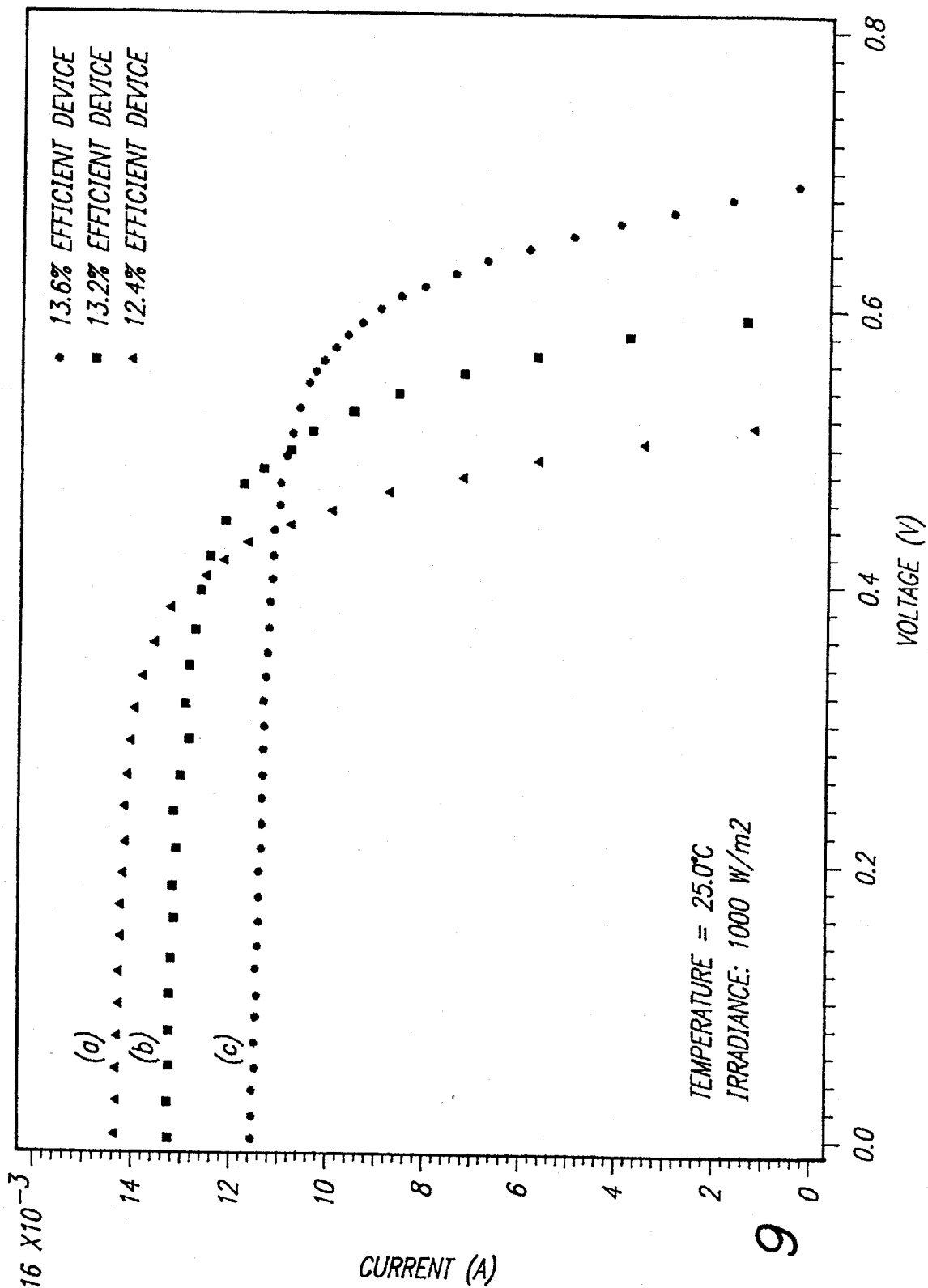


FIG. 9

PREPARATION OF COPPER-INDIUM-GALLIUM-DISELENIDE PRECURSOR FILMS BY ELECTRODEPOSITION FOR FABRICATING HIGH EFFICIENCY SOLAR CELLS

RELATED APPLICATIONS

This application claims the benefit of provisional applications Ser. Nos. 60/044,506 filed Apr. 21, 1997 and 60/004,269 filed Sep. 25, 1995, and is a cjp application of Ser. No. 08/571,150 filed Dec. 12, 1995, now U.S. Pat. No. 5,730,852.

The government has rights in this invention pursuant to National Renewable Energy Laboratory (NREL) contract No. 1326.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of the present invention relates to the preparation of thin film semiconductor devices. More particularly, the present invention relates to electrodeposition of copper-indium-gallium-diselenide films for solar cells.

2. Description of the Related Art

Chalcopyrite ternary thin films of copper-indium-diselenide (CuInSe_2) and copper-indium-gallium-diselenide ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$), both of which are generically referred to as $\text{Cu}(\text{In,Ga})\text{Se}_2$, CIGS, or simply CIS, have become the subject of considerable interest and study for semiconductor devices in recent years. Sulphur can also be, and sometimes is, substituted for selenium, so the compound is sometimes also referred to even more generically as $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ so as to encompass all of these possible combinations. These devices are also referred to as I-III-VI₂ devices according to their constituent elemental groups.

These devices are of particular interest for photovoltaic device or solar cell absorber applications. For photovoltaic applications, the p-type CIGS layer is combined with an n-type CdS layer to form a p-n heterojunction CdS/CIGS device. The direct energy gap of CIGS results in a large optical absorption coefficient, which in turn permits the use of thin layers on the order of 1–2 μm . An additional advantage of CIGS devices is their long-term stability.

Various methods have been reported for fabricating CIGS thin films. Some of the earliest techniques involved heating copper and indium on a substrate in the presence of a selenium-containing gas, including H_2Se . The heating of copper and indium films in the presence of a selenium-containing gas is known as selenization. One drawback to selenizing with H_2Se is that H_2Se gas is highly toxic, thus presenting serious hazards to humans in large scale production environments.

In U.S. Pat. No. 5,045,409, Eberspacher et al. disclose depositing copper and indium films by magnetron sputtering, and depositing a selenium film by thermal evaporation, followed by heating in the presence of various gases. Other methods for producing CIS films have included Molecular Beam Epitaxy, electrodeposition either in single or multiple steps, and vapor deposition of single crystal and polycrystalline films.

Although vapor deposition techniques have been used to yield solar cells with efficiencies as high as seventeen percent (17%), vapor deposition is costly. Accordingly, solar cells made by vapor deposition have generally been limited to devices for laboratory experimentation, and are not suitable for large scale production. On the other hand, thin film

solar cells made by electrodeposition techniques are generally much less expensive. However, solar cells produced by electrodeposition generally suffer from low efficiencies. For example, in *Solar Cells with Improved Efficiency Based on Electrodeposited Copper Indium Diselenide Thin Films*, ADVANCED MATERIALS, Vol. 6 No. 5 (1994), Guillemin et al. report solar cells prepared by electrodeposition with efficiencies on the order of 5.6%.

SUMMARY OF THE INVENTION

Accordingly, it is a general object of this invention to provide an improved process for fabricating high quality thin film $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells.

It is also an object of this invention to provide low cost, high quality thin film solar cells having high conversion efficiencies.

It is a further object of this invention to provide a process for producing Cu—In, Cu—Se, Cu—In—Se, and Cu—In—Ga—Se thin films that have applications in solar and non-solar cells.

It is a still further object of this invention to provide a process for electrodepositing a gallium-containing thin-film solar cell precursor.

To achieve the foregoing and other objects and advantages in accordance with the purpose of the present invention, as embodied and broadly described herein, the process of this invention includes electrodepositing a layer of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$), preferably using direct current in combination with high frequency alternating current. Electrodeposition baths containing 0.1–0.2 molar (M) copper ions, 0.05–0.15M indium ions obtained from indium chloride, 0.05–0.15M gallium ions obtained from gallium chloride, 0.01–0.03M selenium ions, and at least 0.3M lithium chloride were found to produce simultaneous co-electrodeposition of copper, indium, selenium, and appreciable amounts of gallium with a good morphology, when an electrodeposition potential having a high frequency alternating current superimposed upon a DC current was applied. Following simultaneous co-electrodeposition, additional material was vapor deposited to adjust the final composition of the deposited film very close to stoichiometric $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$.

This unique two-step film deposition process allows precursor metal films to be deposited by inexpensive electrodeposition, and then adjusted using the more expensive but more precise technique of physical vapor deposition (PVD) to bring the final film into the desired stoichiometric range. Solar cells may then be completed as for example by chemical bath deposition (CBD) of CdS followed by sputtering of ZnO, and addition of bi-layer metal contacts as well as optional anti-reflective coating.

A solar cell made according to the process disclosed herein achieved a device conversion efficiency of 13.6%. This represents a significant improvement over the 9.4% conversion efficiency device disclosed in U.S. patent application Ser. No. 08/571,150, filed Dec. 12, 1995 now U.S. Pat. No. 5,730,882, of which this application is a continuation-in-part.

The present invention also includes electrodeposition solutions and process parameters whereby gallium may be co-electrodeposited in appreciable amounts along with copper, indium, and selenium, while still obtaining a densely packed, uniform morphology film suitable for processing into a photovoltaic cell. This co-electrodeposition of gallium further decreases the amount of stoichiometry adjustment that must be made by the later PVD step.

Additional objects, advantages, and novel features of the present invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a CIGS photovoltaic device prepared according to the present invention.

FIG. 2 is a cross sectional view of the conducting zinc oxide layer 28 shown in FIG. 1.

FIG. 3 is a scanning electron microscope photograph of the electrodeposited precursor film of Example 1 of the present invention.

FIG. 4 is a graph of the Auger electron spectroscopy analysis for the cell of Example 1.

FIG. 5 is a graph of the Auger electron spectroscopy analysis for the cell of Example 2.

FIG. 6 is a graph of the Auger electron spectroscopy analysis for the cell of Example 3.

FIG. 7 is the x-ray analysis results for the electrodeposited film, and the finished films of Examples 1-3.

FIG. 8 is a graph of the relative quantum efficiency verses wavelength for the cells of Examples 1-3.

FIG. 9 is a graph showing the Current versus Voltage characteristics of the cells of Examples 1-3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention includes an essentially two-step process for fabricating high quality, low cost thin film CIGS semiconductor devices that exhibit photovoltaic characteristics and are especially adaptable for solar cell applications. In the first step, a precursor film of $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$) is electrodeposited on a substrate such as glass coated with molybdenum. This first step may include a unique process and electrodeposition bath for electrodepositing gallium concurrently with other elements, as well as the unique use of an alternating current in conjunction with a direct current.

The second step is physical vapor deposition of copper, indium, gallium, and/or selenium. In this second step the composition of the overall film is carefully controlled so that the resulting thin film is very close to stoichiometric $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$. Both of these steps may be performed on substrates having large surface areas. Accordingly, the process of the present invention allows large area, high efficiency solar cells to be economically produced.

Referring now to FIG. 1, CdS/CIGS photovoltaic device 10 includes a substrate 12 which may be, for example, soda-lime silica glass or amorphous 7059 glass. Substrate 12 further includes a back contact layer 14 of molybdenum, about 1-2 μm thick. The molybdenum may be deposited using DC sputtering from a rotating cylindrical magnetron target (CMAG). To improve adhesion between the Mo layer 14 and the precursor film to be deposited, an additional adhesion layer 16 of copper may also be deposited as by electrodeposition. After Mo layer 14 and optional copper adhesion layer 16 have been deposited, the substrate should be degreased as for example with propanol and dried in flowing nitrogen gas.

A metallic precursor film 18 is then deposited by electrodeposition. The precursor film contains one or more of the elements copper, indium, gallium, and selenium. Elec-

trodeposition is generally a less expensive method of depositing these metals than vapor deposition. However, it is not possible to control the ratios of metals deposited during electrodeposition as precisely as desired. Consequently, prior CIS layers deposited entirely by electrodeposition produced low conversion efficiencies. In the present invention, the electrodeposition step is integrated with the vapor deposition step that follows. This allows precursor metal to be deposited in bulk using an economical electrodeposition step, followed by a vapor deposition step to carefully control the final metal ratios. This results in economical production yet high efficiencies of the resulting cell. The composition of metal precursor film 18 is generally denoted as $\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_n$ ($x=0-2$, $y=0-2$, $z=0-2$, $n=0-3$). The metal precursor film 18 should be deposited to about 1-3 μm thick, with thickness being controlled by coulometric measurements.

It has been found that electrodepositing the films using an AC voltage in addition to a DC voltage produces improved results. An AC voltage improves the morphology of the film. It is also believed that the AC voltage improves nucleation (growth) of the thin film by allowing additional nucleation centers to be created. For an entirely aqueous plating solution, the applicable DC voltage range is approximately 1-5 VDC, with a preferred voltage of approximately 3 VDC. Improved results may be obtained by superimposing an AC voltage of 0.2-5.0 VAC at 1-100 KHz, with preferred values of approximately 3.5 VAC at 10-30 KHz. The plating solution is adjusted to have a pH of approximately 1.0 to 4.0, and more preferably to about 1.4 to 2.4. The plating solution should preferably be at about 10° C. to 80° C., and more preferably at about 24° C. Adding a supporting electrolyte to the plating bath can additionally increase the conductivity of the plating solution, allowing for a further increase in the electrodeposition rate. Salts such as NaCl, LiCl, or Na_2SO_4 have been found to be suitable supporting electrolytes for use with certain embodiments of the present invention.

In completely aqueous solutions, electrolysis of water molecules begins to occur to an undesirable extent at voltage levels that are too high. The resulting O^{2-} and OH^- ions combine with deposition metal ions or deposited metal to form unwanted metal oxides and hydroxides on the precursor film 18. To overcome this disadvantage, the water in the plating solution may be either partially or completely replaced by one or more organic solvents such as dimethyl sulfoxide (DMSO). Increasing the organic solvent content of the electrodeposition solution allows the cathodic potential to be increased without unacceptable increases in metal oxide and hydroxide formation rates. The increased cathodic potential increases the deposition rate of the precursor films. An additional advantage is that increasing the cathodic potential increases the deposition rate of gallium relative to the deposition rates of other deposited metals. Therefore, using a solution containing one or more organic solvents allows the cathodic potential to be selected from a wider range so as to achieve a more desired stoichiometry of the as-deposited precursor film 18. When an organic solvent is used, the preferred cathodic potential is approximately 3-10 VDC and 0.2-5.0 VAC at approximately 1-100 KHz. Value of approximately 5 VDC and 0.45 VAC at approximately 18.1 KHz were found to yield good results.

As the number of elements to be simultaneously electrodeposited increases, the difficulties increase. Obtaining simultaneous electrodeposition of four elements in pre-defined ratios with good morphology, for example, can be an extremely difficult task. The parameters that must be simultaneously adjusted include but are not limited to: total

solution molarity, relative molarities of constituents, from which compounds to obtain the desired constituent elements, pH, temperature, voltage, waveform characteristics, and electrolytic fluid. Because of the complexities involved in simultaneous co-electrodeposition, it is believed that gallium had never before been successfully co-electrodeposited along with copper, indium, and selenium to produce a photovoltaic device. The present invention includes solutions and process parameters whereby gallium may be co-electrodeposited in appreciable amounts along with the other three constituent elements of CIGS.

If desired, a second electroplating solution may be employed to adjust the stoichiometry of the electrodeposited film prior to the vapor deposition phase. For example, a first electrodeposition step may produce a CIGS precursor film with less gallium than optimally desired. Although the gallium content can be increased during the vapor deposition phase, it may be less expensive to deposit a certain amount of gallium using a second electrodeposition solution to make a coarse stoichiometric adjustment prior to proceeding to fine stoichiometric adjustment at the vapor deposition step. Another potential motivation for using a second electrodeposition solution is to achieve a composition gradient in the deposited film, as suggested by U.S. Pat. No. 4,335, 266 issued to Michelsen et al. which is hereby incorporated by reference for its teachings of composition-graded CIGS thin films for solar cell and other applications. Yet another way of achieving composition grading during electrodeposition is to vary process parameters such as cathodic potential, ionic concentrations, pH, or temperature, as electrodeposition proceeds.

Several examples of electrodeposited precursor films fabricated according to the present invention are given. These examples include Cu—In—Ga—Se, In—Se, Cu—Se, and Cu—In—Se, precursor films. The solution for co-depositing all four elements includes ions of each of the elements of copper, indium, gallium, and selenium. The metal ions may be supplied in the form of dissolved metal salts. For precursor films that do not contain gallium, gallium should be added to raise the energy gap.

In the discussion and claims that follow, electrodeposition potential is expressed in terms of a voltage without specifying positive or negative voltage.

It is to be understood that the substrate or working electrode on which the thin film is to be deposited is to be connected as the electrodeposition cathode, with the counter electrode being connected as the anode. Accordingly, the electrodeposition voltages discussed herein are to be understood as negative voltages. In accordance with this convention, where electrodeposition voltages are expressed as, e.g., "at least 1.0 volt", this indicates that an electrodeposition voltage that is at least as negative as -1.0 volt with respect to the counter electrode is to be applied to the substrate. Discussing the electrodeposition voltages as unsigned voltages is to be understood as merely a shorthand way of referring to the absolute potential difference between the electrodes.

After the precursor film 18 has been electrodeposited it should be cleaned. A suitable method is to rinse precursor film 18 with deionized water and dry it in flowing nitrogen gas. After precursor film 18 has been cleaned, an additional layer 20 of copper, indium, gallium, and/or selenium, is deposited by physical vapor deposition to adjust the final film composition to the ratios of approximately Cu=1-1.2: (In, Ga)=1-1.2: Se=2-2.5, and most preferably to approximately 1:1:2. That is, the final film composition is adjusted

to approximately $\text{Cu}_1(\text{In,Ga})_1\text{Se}_2$, which is to say $\text{Cu}_1(\text{In}_{1-x}\text{Ga}_x)_1\text{Se}_2$ where x is within the range of 0 to 1, inclusive. By controlling the ratio of In/Ga the energy gap between the CdS and the CIGS layers can be adjusted to the optimal or nearly optimal value. An energy gap of approximately 1.45 eV is considered optimal for terrestrial solar energy conversion, and is achieved by an In/Ga ratio of approximately 3:1. For cells prepared according to the method disclosed herein, a Ga/(In+Ga) atomic ratio of 0.34-0.50 is preferred, with a ratio of 0.39 producing the highest observed efficiency. The substrate (precursor film) temperature should be 300° C. to 600° C. during PVD, and preferably about 550° C.

After PVD, the films should then be annealed. Annealing improves the homogeneity and quality of the films. A high quality CIGS film is one that does not exhibit an excessive amount of copper nodules, voids, or vacancies in the film which would reduce conversion efficiencies. Annealing the films at 250° C. to 500° C. in a vacuum, followed by slow cooling at a rate of approximately 3° C./min to avoid thermal shock was found to yield good results. Because selenium has a much higher vapor pressure than either copper, indium, or gallium, selenium may be lost from the film during the high temperature steps of vapor deposition and annealing. To compensate, the atmosphere during these steps may contain a moderate overpressure of selenium. In the preferred embodiment, the film is selenized at a rate of 5-100 Å/s during cool-down from PVD temperature to annealing temperature.

Once the CIGS layers 18 and 20 collectively are deposited and annealed, a thin layer 22 of n-type semiconductor comprising cadmium sulfide is deposited next. CdS layer 22 is preferably deposited by chemical bath deposition (CBD) to a thickness of approximately 200-1000 Å. The CBD bath may be prepared from 0.08 gm CdSO_4 , 2.5 gm thiourea, and 27.5 gm NH_4OH dissolved in 200 ml water. The deposition temperature should be approximately 40°-80° C.

A layer 28 of conducting wide bandgap n-type semiconductor materials is deposited next. In the preferred embodiment, layer 28 comprises two zinc oxide layers 24 and 26 as shown in FIG. 2. First zinc oxide layer 24 is deposited with RF sputtering at approximately 0.62 watts/cm² in an argon plasma at 10 millitorrs pressure. Second zinc oxide layer 26, comprising approximately 1-5% Al_2O_3 -doped zinc oxide, is also prepared using RF sputtering at approximately 1.45 watts/cm² in an argon plasma at 10 millitorrs pressure. In an exemplary embodiment the resistivity of the first layer was 50-200 ohm/cm², and resistivity of the second layer was 15-20 ohm/cm². The transmissivity of the overall ZnO layer was 80-85%.

Bi-layer metal contacts 30 may then be prepared with an e-beam system or other techniques. In an exemplary embodiment a first metal contact layer was 500-1000 Å thick Ni and the second metal contact layer was 1-3 μm thick Al. Metal contacts 30 will generally be laid out in fine grid lines across the collecting surface of the device and connected to a suitable current collecting electrode (not shown). The efficiency of the resulting device can be further increased by adding an antireflection coating 32, such as a 600-1000 Å layer of MgF_2 by electron beam. A device prepared according to Example 3 below exhibited a conversion efficiency of 13.6%.

EXAMPLE 1

A thin film containing copper, indium, gallium, and selenium was deposited onto a glass substrate coated with

approximately 500 Å Mo, and processed into a photovoltaic cell. The thin film was obtained by preparing a solution containing ions of copper, indium, and selenium, and further including ions of gallium in a concentration of at least 0.05 molar, and at least 0.3 molar LiCl. More particularly, the electrodeposition bath comprised 2.1286 gm Cu(NO₃)₂·H₂O, 7.9625 gm InCl₃, 1.3929 gm H₂SeO₃, and 9.2063 gm Ga(NO₃)₃, and 14.08 gm LiCl dissolved in 450 ml of water. The resulting bath comprised approximately 0.014M copper, 0.08M indium, 0.08M gallium, and 0.023M selenium ions. The pH was adjusted to 1–2. Deposition proceeded at 24° C.

The substrate was employed as the working electrode, and platinum gauze was used as the counter electrode in a two electrode system. The electrodeposition voltage comprised a DC component of at least 0.5 volt. More particularly, the electrodeposition voltage comprised a DC voltage of at least 1.0 volt and an AC voltage of at least 0.5 V at a frequency of at least 1.0 KHz superimposed thereon. Still more particularly, the electrodeposition voltage comprised a DC component of 3.0 volts, and an AC component of 3.5 volts pulsed at 20 KHz superimposed thereon. The voltage was supplied by a power source obtained from Team Specialty Products Corporation of Albuquerque, N.M. The AC component is nominally a square wave. However, due to the complex impedances of the power supply and the remainder of the electrodeposition equipment operating at 20 KHz, it will be understood that the voltage as measured at the substrate will not be a perfect square wave. Thus, the applied voltage is more properly described using the broader term of AC "pulsed" rather than the narrow term of a "square wave". This convention will be maintained throughout this disclosure and appended claims. The resulting as-deposited precursor layer had a composition of Cu_{1.00}In_{0.34}Ga_{0.02}Se_{0.91}. FIG. 3 is a scanning electron microscope photograph of the as-deposited film. The photograph shows the film to be tight, densely packed, and uniform.

After electrodeposition, additional In, Cu, Ga, and/or Se were added to the film by physical evaporation to adjust the final composition to CuIn_{1-x}Ga_xSe₂, with the ratio of Ga/(In+Ga) being 0.16. The films were allowed to crystallize at 550° C. for five minutes. The substrate (precursor film) temperature during the physical evaporation step was also 550° C. The film was then selenized by exposure to selenium vapor during the cool-down time, with cooling at approximately 20° C. per minute.

FIG. 7 is the X-ray analysis results for the electrodeposited film, and the finished films of Examples 1–3. The X-ray analysis of the as-deposited precursor film indicates the presence of both the CIGS phase and the Cu₂Se phase. The X-ray analysis of the film after final film composition adjustment shows only the CIGS phase. The shifts in 2-theta values are due to different Ga concentrations in the absorber layers.

Photovoltaic devices were completed by chemical bath deposition of approximately 500 Å CdS followed by radio frequency sputtering of 500 Å intrinsic ZnO and 3500 Å of Al₂O₃-doped ZnO. Bilayer Ni/Al top contacts were deposited using an e-beam system. An anti-reflection coating of 100 nm of MgF₂ was applied as the final step.

The device was evaluated at AM1.5 illumination (1000 W/m², 25° C., ASTM E892 global). The device was also characterized by Auger electron spectroscopy (AES). FIG. 4 is the AES analysis results for the finished photovoltaic cell showing the atomic distribution of the film at varying depths within the film. FIG. 8 shows the relative quantum efficiency of the cell as a function of wavelength. FIG. 9 shows the

Current versus Voltage characteristics of the finished cell. The cell exhibited an overall efficiency of 12.4%. Other performance parameters for this cell are listed in Table 1 below.

EXAMPLE 2

A cell was prepared according to Example 1, but the PVD step was conducted to adjust the final Ga/(In+Ga) ratio to 0.26 rather than 0.16. The device efficiency improved from 12.4% to 13.2%. The AES analysis is shown in FIG. 5. The relative quantum efficiency is shown in FIG. 8. The Current vs. Voltage performance is shown in FIG. 9.

EXAMPLE 3

A cell was prepared according to Example 1, but the PVD step was conducted to adjust the final Ga/(In+Ga) ratio to 0.39. The overall device efficiency improved to 13.6%. The AES analysis is shown in FIG. 6. The relative quantum efficiency is shown in FIG. 8. The Current vs. Voltage performance is shown in FIG. 9. Performance parameters for the cells of Examples 1–3 are given in Table 1 below.

TABLE 1

Example	Ga (In + Ga)	Area (cm ²)	V _{OC} (mV)	J _{SC} (mA/cm ²)	Fill Factor (%)	Total-Area Efficiency
1	0.16	0.413	521	34.9	68.2	12.4
2	0.26	0.420	602	31.7	69.4	13.2
3	0.39	0.419	689	27.6	71.6	13.6

Performance Parameters for Photovoltaic Cells of
Examples 1–3

EXAMPLE 4

A bath containing approximately 0.016M Cu(NO₃)₂·H₂O, 0.08M InCl₃, 0.08M H₂SeO₃, and 0.024M Ga(NO₃)₃ (relative ratios of approximately 1, 5, 5, and 1.5, respectively) was prepared at a pH of 1.6. Electrodeposition proceeded at at least 2.0 volts DC and at least 2.0 volts AC at a frequency of at least 10 KHz superimposed thereon. More particularly, electrodeposition proceeded at 3.0 VDC with a pulsed AC voltage of 3.5 volts at a frequency of 20 KHz superimposed thereon. ICP compositional analysis revealed the following film compositions before and after the precursor film was finished:

As-Deposited: Cu_{1.00}In_{0.36}Ga_{0.03}Se_{1.00}

After PVD adjustment: Cu_{1.00}In_{1.04}Ga_{0.18}Se_{2.22}

Note that the as-deposited film contains the highest gallium content of any of the examples presented herein.

A photovoltaic device was completed as before, with the final Ga/(In+Ga) ratio adjusted to approximately 0.3. The final efficiency of the device was 12.3%.

EXAMPLE 5

An electrodeposition bath was prepared by dissolving 1.9956 gm Cu(NO₃)₂·H₂O, 9.9531 gm InCl₃, 1.7411 gm H₂SeO₃, and 12.0832 gm Ga(NO₃)₃, and 15 gm LiCl in 450 ml of water (0.18M copper ions, 0.10 indium ions, 0.105M gallium ions, and 0.29M selenium ions). Electrodeposition proceeded at a voltage of 3.00 VDC and 3.53 VAC superimposed thereon. The composition of the as-deposited precursor layer, expressed as 10¹⁶ atoms/cm², was Cu_{1.00}In_{0.46}Ga_{0.01}Se_{1.16}. The precursor layer was completed

by PVD. The finished device exhibited a conversion efficiency of 12.3%.

EXAMPLE 6

A metallic precursor film of $\text{In}_{1-2}\text{Se}_{1-3}$ was electrodeposited on glass substrates coated with a Mo or Mo/Cu layer approximately 500 Å thick. The precursor film was deposited using an electroplating solution containing 2.25 gm InCl_3 and 0.41 gm H_2SeO_3 dissolved in 200 ml of water. The pH of the solution was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. The films were 1–3 μm thick and adhered to the substrate.

EXAMPLE 7

A metallic precursor film of $\text{Cu}_{1-2}\text{Se}_{1-3}$ was electrodeposited on a substrate using an electroplating solution containing 6.21 gm $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.16 gm H_2SeO_3 dissolved in 300 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate.

EXAMPLE 8

A metallic precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Se}_{1-3}$ was electrodeposited on a substrate using an electroplating solution containing 4.47 gm CuCl_2 , 5.67 gm InCl_3 and 3.39 gm H_2SeO_3 dissolved in 1050 ml water. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate. The electrodeposited film was slightly indium poor. Indium was then added by vapor deposition to adjust the final content to approximately CuInSe_2 . CdS and ZnO were then added to complete the solar cell. The resulting solar cell was exposed to ASTM E892-87 Global (1000 Wm^{-2}) standard irradiance spectrum at 25° C. Performance parameters for the finished solar cell, having an area of 0.4285 cm^2 , were measured as:

$V_{OC} = 0.4138 \text{ V}$	$V_{Pmax} = 0.3121 \text{ V}$
$I_{SC} = 15.40 \text{ mA}$	$I_{Pmax} = 12.96 \text{ mA}$
$J_{SC} = 35.94 \text{ mA cm}^{-2}$	$P_{max} = 4.045 \text{ mW}$
Fill Factor = 63.47%	Efficiency = 9.44%

The device contained only Cu—In—Se, without any gallium. The device exhibited an efficiency of 8.76% without antireflective coating, and 9.44% after an antireflective coating was added.

EXAMPLE 9

A precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ was electrodeposited using a solution containing 1.12 gm $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 12.0 gm InCl_3 , 4.60 gm $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 1.80 gm H_2SeO_3 dissolved in 450 ml of water. This is equivalent to approximately 2.49 gm/l $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 26.7 gm/l InCl_3 , 10.2 gm/l $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 4.0 gm/l H_2SeO_3 , and approximately 0.0084, 0.12, 0.28, and 0.31 molar of copper, indium, gallium, and selenium ions, respectively. The pH was adjusted between 1.4 and 2.4 using dilute HCl (10% by

volume). The films were deposited by applying a 2–5 V direct current voltage in combination with an alternating current voltage of 0.45 V at 18.1 KHz frequency. As deposited layers were 1–3 μm thick and adhered to the substrate.

EXAMPLE 10

A precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , and 7.192 gm $\text{Ga}(\text{NO}_3)_3$ dissolved in 450 ml of DMSO. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

EXAMPLE 11

A precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , and 7.192 gm $\text{Ga}(\text{NO}_3)_3$ dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

EXAMPLE 12

A precursor film of $\text{Cu}_{1-2}\text{In}_{1-2}\text{Ga}_{0.01-1}\text{Se}_{1-3}$ was electrodeposited using a solution containing 1.496 gm $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, 14.929 gm InCl_3 , 1.523 gm H_2SeO_3 , 7.192 gm $\text{Ga}(\text{NO}_3)_3$, and 10 gm Na_2SO_4 , and 20 gm LiCl dissolved in a mixture of 400 ml DMSO and 50 ml water. The films were deposited at 25° C. and also at 50° C. at an applied voltage of 5 VDC.

The present invention as described above may be incorporated in a variety of applications, as for example the conversion of solar energy to electric energy for baseline power generation. Other applications include appliances such as solar-powered calculators, battery charges such as those used with freeway emergency call boxes, photoelectric eyes, night security light activators, light meters for photographic and other purposes, and the like.

Although the present invention has thus been described in detail with regard to the preferred embodiments and drawings and examples thereof, it should be apparent to those skilled in the art that various adaptations and modifications of the present invention may be accomplished without departing from the spirit and the scope of the invention. Accordingly, it is to be understood that the detailed description and the accompanying drawings as set forth hereinabove are not intended to limit the breadth of the present invention, which should be inferred only from the following claims and their appropriately construed legal equivalents.

What is claimed is:

1. A process for preparing a copper-indium-gallium-diselenide film, the process comprising the steps of:

providing a substrate;

providing an electrodeposition bath containing ions of copper, indium, and selenium, the bath further containing ions of gallium in a concentration of at least 0.05 molar;

inserting said substrate into said electrodeposition bath; forming a semiconductor layer by simultaneously electrodepositing a film comprising copper, indium, selenium and gallium from said electrodeposition bath onto said substrate, the electrodeposition proceeding at an applied electrodeposition voltage of at least 0.5 volt; and

depositing by physical vapor deposition additional material selected from the group consisting of copper,

11

indium, gallium, and selenium, onto said semiconductor layer to achieve a final stoichiometry for said semiconductor layer and said additional material, combined, of approximately $\text{Cu}_1(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ where x is within the range of 0 to 1, inclusive.

2. The process of claim 1 wherein x is greater than approximately 0.34.

3. The process of claim 1 wherein said gallium ions are obtained from gallium nitrate.

4. The process of claim 3 wherein said electrodeposition bath further comprises at least 0.3 molar lithium chloride.

5. The process of claim 1 wherein:

said indium ions are obtained from indium chloride.

6. The process of claim 1 wherein:

said electrodeposition voltage comprises a DC voltage of at least 1.0 volt and an AC voltage of at least 0.5 V at a frequency of at least 1.0 KHz superimposed thereon.

7. The process of claim 6 wherein:

said AC voltage consists of a pulsed voltage.

8. The process of claim 7 wherein said AC voltage frequency is at least 10 KHz.

9. The process of claim 8 wherein said DC voltage is at least 2 volts, and said AC voltage is at least 2 volts.

10. A process for preparing a photovoltaic device gallium-containing precursor film, the process comprising the steps of:

providing a substrate;

providing an electrodeposition bath containing ionic copper, indium, and selenium, and gallium in the approximate relative ratios of 1, 5, 1.5, and 5, respectively;

inserting said substrate into said electrodeposition bath; and

forming a thin film layer by simultaneously electrodepositing copper, indium, selenium and gallium from said electrodeposition bath onto said substrate.

11. The process of claim 10 further comprising the step of: depositing by physical vapor deposition additional material selected from the group consisting of copper,

12

indium, gallium, and selenium, onto said thin film layer to achieve a final stoichiometry for said thin film layer and said additional material, combined, of approximately $\text{Cu}_1(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ where x is within the range of 0 to 1, inclusive.

12. The process of claim 10 wherein:

said electrodeposition proceeds at an electrodeposition potential comprising a DC component of at least 0.5 volt.

13. The process of claim 12 wherein:

said electrodeposition potential further comprises an AC component of at least 1.0 volt at a frequency of at least 1 KHz.

14. The process of claim 12 wherein said electrodeposition potential further includes an AC component of at least 0.5 volt.

15. A process for preparing a photovoltaic device gallium-containing precursor film, the process comprising the steps of:

providing a substrate;

providing an electrodeposition bath comprising approximately 0.01–0.02M copper ions, 0.05–0.15M indium ions, 0.05–0.15M gallium ions, and 0.01–0.03M selenium ions

inserting said substrate into said electrodeposition bath; forming a metal-containing film by simultaneously electrodepositing at least three elements from said electrodeposition bath onto said substrate; and

depositing by physical vapor deposition additional material selected from the group consisting of copper, indium, gallium, and selenium, onto said metal-containing film to achieve a final stoichiometry for said metal-containing film and said additional material, combined, of approximately $\text{Cu}_1(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ wherein x is within the range of approximately 0.34 to 0.50.

16. The process of claim 15 wherein said electrodeposition bath further comprises at least 0.3M lithium chloride.

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<p>13. ABSTRACT (<i>Maximum 200 words</i>): This report describes our scientific understanding of the CIGS materials system, solar cells, and processes. Through DOE support, the investigators developed much of the technology and device fabrication infrastructure applied to electrodeposited (ED) materials. The electrodeposition process is simple and fast, and can synthesize multinary precursors for subsequent processing into $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) thin-film absorbers for solar cells. The device fabricated by using electrodeposited CIGS precursor layers resulted in total-area conversion efficiencies up to 15.4%. As-deposited precursors are Cu-rich CIGS. Additional In, Ga, and Se (up to 50%) are added to the precursor films by physical vapor deposition (PVD) to adjust the final semiconductor film composition to about $\text{Cu}_{0.95}\text{In}_{0.75}\text{Ga}_{0.25}\text{Se}_2$. The ED device parameters are compared with those of an 18.8% PVD device. The tools used for comparison are current-voltage, capacitance-voltage, and spectral response characteristics. The individual parameters of the device prepared from ED precursor films showed no significant deterioration from those of the PVD CIGS cells.</p> <p>We also developed a buffer-based electrodeposition bath. Using the buffer solution enhances the stability of the electrodeposition process, and no metal oxides or hydroxides precipitate out of the solution. The buffer-based bath also deposits more gallium in the precursor films. As-deposited precursors are stoichiometric or slightly Cu-rich CIGS. Only a minimal amount (5%-10% of total materials) of indium was added to the ED precursor films by PVD to obtain a 9.4%-efficient device.</p> <p>In general, the films and devices have been characterized by inductively coupled plasma spectrometry, Auger electron spectroscopy, X-ray diffraction, electron-probe microanalysis, current-voltage, capacitance-voltage, and spectral response.</p>				
14. SUBJECT TERMS: PV; $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS); electrodeposition process; Auger electron spectroscopy (AES); X-ray diffraction (XRD), electron-probe microanalysis; current-voltage; capacitance-voltage; spectral response; buffer-based bath; conversion efficiency		15. NUMBER OF PAGES		
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